Aggregation Structure and Thermal Conductivity of Nanofluids

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Nanofluids are obtained by suspending metallic nanoparticles in conventional base liquids. Such a new class of heat-transfer fluid is superior to the base liquids in energy-transport performance, which depends on the distribution, volume fraction and thermal properties of the suspended nanoparticles. The theory of Brownian motion and the diffusion-limited aggregation model are applied to simulate random motion and the aggregation process of the nanoparticles. A theoretical model is developed to predict the thermal conductivity of nanofluids. Comparison between the theoretical and experimental results shows the validity and accuracy of the theoretical model.

Introduction

Development of the nanomaterial technology makes it possible to structure a new type of heat-transfer fluid by suspending nanoparticles in conventional liquids. Choi (1995) used the term *nanofluid* to refer to this class of fluids. The nanoparticles suspended in a base liquid are in random motion under the influence of several acting forces, such as the Brownian force and the London–Van der Waals force. The random motion of the suspended nanoparticles strengthens energy transport inside the liquid. Some experiments revealed that the dimensions, volume fraction, properties of the nanoparticles, and the particle distribution affect the heat-transfer characteristic of the nanofluid (Xuan and Li, 2000). Such unique properties of the suspended nanoparticles stimulate more and more investigations on the mechanism of energy transport enhancement.

During the stochastic motion of the suspended nanoparticles, aggregation and dispersion may occur among nanoparticle clusters and individual nanoparticles. Under the influence of the external and internal forces, the suspended nanoparticles may experience interparticle collision and attachment of the colliding particles and form aggregates. Gregory (1996) described the mechanism of particle aggregation and types of interaction along with the aggregation process in detail. It is well known now that aggregates can be treated as fractal objects (Meakin, 1988). The fractal dimension is a suitable parameter for marking aggregate structure, and one can find a variety ways of defining the fractal dimension in the literature. According to their observation upon some transmission electron micrographs of clusters of gold colloids, Weitz and Huang (1984) concluded that the structures of gold nanoparticles clusters exhibit a ramified complex structure and should be analyzed in terms of fractals. As shown in Figure 1, the copper nanoparticles suspended in the base liquid (water) also possess the statistically fractal structure.

According to the Brownian theory, the smaller the sizes of the colloid particles, the faster the particles move, so that energy transport inside the liquid becomes stronger. The clusters consisting of more than two nanoparticles move slower than a single nanoparticle. Furthermore, the clusters may sedimentate under the gravity if the clusters grow large enough. Thus, the enhancement intensity of energy transport from the nanoparticles will decrease in cases where more clusters arise inside the nanofluid. The distribution structure of the suspended nanoparticles is one of the main factors affecting the thermodynamic properties of the nanofluid besides the nanoparticle diameter and volume fraction. So far some experimental investigations have been carried out to determine thermal conductivity of nanopaticle–liquid suspensions (Choi, 1995; Xuan and Li, 2000), but little theoretical work has been done to predict such a parameter while taking the effect of the morphology of nanofluids into account. The purpose of the present work is to investigate the random motion process and distribution structure of the suspended nanoparticles and to analyze the enhancement mechanism of energy transport from the nanoparticles. A thermal model is proposed that considers the effects of the volume fraction of the nanoparticles and the morphology of the nanofluid on the energy transport process. An analytical ex-

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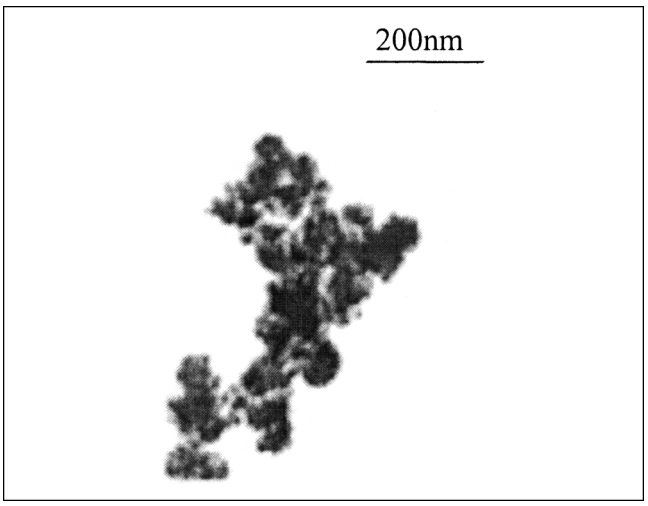

Figure 1. Electron microscopy (TEM) photo of Cu–water nanofluid ($r = 10$ nm, $\phi = 2.0\%$).

pression for predicting the thermal conductivity of nanofluids is developed and its applicability is verified by the agreement of the theoretical results with the experimental ones.

Aggregation Simulation and Fractal Dimension

The nanoparticles suspended in a base liquid are driven to stochastic motion by rapidly fluctuating forces resulting from the bombardment of the ambient solvent molecules. It is this random motion of the nanoparticles that exerts important and even dominant effects on the morphology of the nanofluid and energy transport inside the nanofluid. Random motion of the nanoparticles may be the main reason that the characteristics of the nanofluid are quite different from those of the conventional liquid–solid mixtures with particles of μm or even mm diameters. According to Langevin's theory (Probstein, 1994), the forces acting on the nanoparticles can be divided into two parts: the frictional drag force and the random forces. The stochastic motion of the nanoparticle of mass m_i can be described dynamically by Langevin's equation

$$m_i \frac{d^2x}{dt^2} = -a\frac{dx}{dt} + F(t) + F_w \tag{1}$$

The averaged value of the random force, $F(t)$, can be neglected without loss of generality. In the case with no field force, F_w, application of the energy equipartition principle yields

$$\overline{x^2} = \frac{2k_BT}{m\left(\frac{a}{m}\right)^2}\left[\frac{a}{m}t + e^{-(a/m)t} - 1\right] \tag{2}$$

where the Boltzmann constant $k_B = 1.381 \times 10^{-23}$ J/K.

For a spherical particle of radius r suspended in a liquid with the viscosity η, the Stokesian relation indicates the frictional coefficient $a = 6\pi r\eta$. Equation 2 can further be simplified under certain conditions. For Cu nanoparticles ($r = 20$ nm) at room temperature, for example, Eq. 2 can be approximated as

$$\overline{x^2} \approx \frac{k_BT}{3\pi r\eta}t \tag{3}$$

It is clear that the statistically averaged square value of particle displacement is proportional to time and temperature, but inversely proportional to the particle radius and the fluid viscosity.

While the suspended nanoparticles are in Brownian motion, some particles may collide with each other, and particle aggregation may occur. Thus, particle clusters can result from collision among the nanoparticles. Aggregation and dispersion of the particles, as well as cluster formation, are controlled by a variety of internal potentials between the base liquid and nanoparticles, and among the particles and some external forces. Aggregate formation of the nanoparticles inside a base liquid has the typical feature of particle–particle, particle–cluster, and cluster–cluster aggregation, so that nanoparticle aggregation belongs to the diffusion-limited aggregation (DLA), and the conventional DLA model (Gauthier et al., 1993) can be used to describe the aggregation process of the suspended nanoparticles and the morphology of the nanofluid.

The random motion of nanoparticles is so fast that a particle experiences stochastic displacement once within a range of 10^{-9} s even 10^{-12} s. In the case where the number of nanoparticles, N, is very large, it is very difficult to conduct a real-time simulation of the motion process of all nanoparticles. An aggregation simulation procedure similar to those used by Weitz and Huang (1984) and Gauthier et al. (1993) is adopted for computer simulation of particle–particle, particle–cluster, and cluster–cluster aggregation inside the nanofluid. For a three-dimensional simulation, a cube represents a container and the volume fraction of the nanofluid varies with the number and radii of nanoparticles contained in the cube. The time step is determined with the particle radius, according to the theory of Brownian motion. Within a time step, the displacement of a nanoparticle is set to be equal to the particle diameter. At the initial state the nanoparticles are assumed to be evenly distributed in the whole container and each particle or cluster moves once within one time step. A displacement is divided into four sections in order to keep the particles from overlapping. The displacement is as follows: a nanoparticle is arbitrarily chosen from the particle mixture and its initial position is given, the displacement section is obtained according to the particle radius or the radius of gyration of the particle cluster, and then the terminal position of the nanoparticle or cluster after the displacement is determined. While simulating the entire displacement, the particle or cluster moves toward the terminal position section by section. Within each section, it is estimated whether the particle or the cluster collides with other particles or clusters. Once nanoparticles and/or clusters collide with each other, attachment or aggregation between these particles and/or clusters takes place, which ends the displacement simulation for this particle or cluster; otherwise, simulation corresponding to the next section continues until the terminal position is reached. Then, another particle or cluster is chosen and its

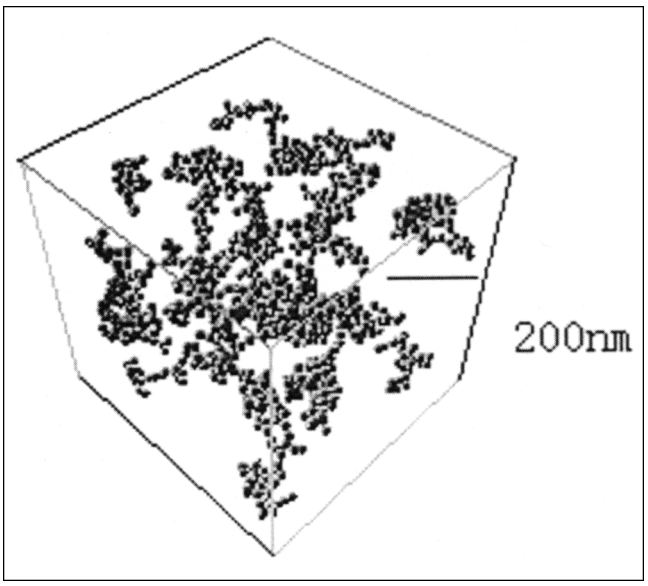

Figure 2. Simulated aggregation structure of Cu–water nanofluid ($r = 10$ nm, $\phi = 2.0\%$).

displacement simulation follows the same procedure. These processes continue until all the single nanoparticles and clusters in the mixture move once. Then, displacement of the nanoparticles or clusters corresponding to the next time step begins. All the nanoparticle clusters as well as the nanoparticles contained in a cluster are counted throughout the simulation.

The length of time that diffusion lasts is the dominant factor causing a collision among nanoparticles and/or clusters. Clusters may precipitate or sedimentate once the aggregates grow to some threshold size. To simulate the aggregation behavior of nanoparticles, Weitz and Huang (1984) introduced the assumption that a natural limit to the diffusive behavior of particles clustering is when the time it takes for the particles to diffuse a mean interparticle distance equals the time it takes for them to drift that same distance due to gravitational forces. One can also assume that once a cluster is large enough and the number of nanoparticles contained in the cluster is larger than a given threshold, the cluster will break into several smaller ones in order to avoid unlimited cluster growth. The threshold limit can be obtained from a random number generator.

Figures 1 and 2 show, respectively, the transmission electron micrograph and a computer simulation image of the aggregates of the nanoparticles suspended in nanofluid consisting of water and Cu–nanoparticles, in which the mean radius of single nanoparticles is 10 nm and the volume fraction is 2.0%. The simulated result reveals an aggregation structure similar to that in the TEM photo of the experiment. Evidently, the shapes of nanoparticle clusters become irregular and complex because of the stochastic Brownian motion of the nanoparticles. The clusters distributed in the liquid have a statistically self-similar feature. All these cluster branches are open and have no obvious geometrical center.

According to the definition of the fractal dimension, there are different approaches for determining this value. Here the approach described by Gregory (1996) is used and the concept of the radius of gyration of a cluster is introduced to represent the size of a cluster. Consider the cluster (or aggregate) consisting of N nanoparticles. The fractal dimension D_f relates to the number of nanoparticles contained in the cluster to the radius of gyration, R_s, of the cluster as follows

$$N \propto R_s^{D_f} \tag{4}$$

The dimensionless radius of gyration of the cluster is defined by

$$R_s = \left(\sum_{i=1}^{N} \frac{L_i^2}{N \times r^2} \right)^{1/2} = \left[\sum_{i=1}^{N} \frac{(x_i - x_G)^2 + (y_i - x_G)^2 + (z_i - x_G)^2}{N \times r^2} \right]^{1/2} \tag{5}$$

where r is the radius of nanoparticles, and L_i is the distance between nanoparticle i and the center of gravity $G(x_G, y_G, z_G)$ of the cluster.

If Eq. 4 applies over a wide range of aggregate sizes, it implies that the aggregates are of a self-similar structure, which is independent of the scale of observation. Since various forms of clusters consisting of N nanoparticles consistent with the scale of observation may exist, R_s can be defined as the averaged dimensionless radius of gyration of the clusters. From Eq. 4, one can obtain

$$\ln N = D_f \times \ln R_s + C \tag{6}$$

In the dual-logarithm coordinate system, the numerical calculation results in a series of points $(\ln R_s, \ln N)$ by choosing the scales of different radii. A straight line is obtained by the minimum-square method and the slope of the line in the log–log plot corresponds to the value of the fractal dimension, D_f (as shown in Figure 3). A lower fractal dimension indicates a more open aggregate structure. On the other hand, the mean dimensionless radius R_c of gyration of the clusters

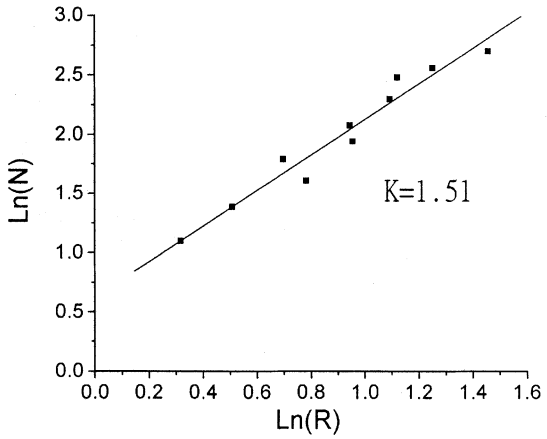

Figure 3. Determination scheme of the fractal dimension.

is obtained by means of Eq. 6. In such a case, the apparent radius r_c of the clusters is given as

$$r_c = rR_c \tag{7}$$

Obviously, its value depends upon the structure of the nanoparticles aggregates, that is, the fractal dimension. One can gain insight into the morphology of the nanofluid from computer simulation of aggregation.

Thermal Conductivity Simulation of the Nanofluid

As mentioned before, the suspended nanoparticles enhance energy transport inside the nanofluid. The reason can be explained by the following two aspects: the first is that the suspended nanoparticles alter the fluid composition and make the original base liquid into a suspension, thus, affecting the energy transport process, which corresponds to the first term on the righthand side of Eq. 8; the second aspect is that the random motion of the suspended nanoparticles as well as the interfacial interactions among the particles and the liquid molecules enhance energy transport inside the liquid, which refers to the second term on the righthand side of Eq. 8. It is assumed that both of these modes of energy transport are completely separable. Thus, the total energy flux of a nanofluid system can be written as

$$\boldsymbol{q}_{\text{eff}} = \boldsymbol{q}_m + \boldsymbol{q}_f \quad \text{or} \quad -k_{\text{eff}}\nabla T = -k_{\text{eff},m}\nabla T - k_{\text{eff},f}\nabla T \tag{8}$$

A number of publications exist that deal with the thermal conductivity of conventional solid–liquid mixtures (Hamilton and Crosser, 1962; Leal, 1977; Maxwell, 1954; Rocha and Acrivos, 1973). All these paid no attention to the effects of arbitrary motion of the suspended particles and of the structure of aggregates inside the mixtures. Among them, Maxwell's expression is introduced to calculate the component, $k_{\text{eff},m}$

$$\frac{k_{\text{eff},m}}{k_f} = \frac{k_p + 2k_f - 2\phi(k_f - k_p)}{k_p + 2k_f + \phi(k_f - k_p)} \tag{9}$$

where k_f and k_p are the actual thermal conductivity of the base liquid and the nanoparticle material, respectively.

The random motion of the suspended nanoparticles must be taken into account in order to obtain an expression for the component $k_{\text{eff},f}$. Although some researchers (Pitchumani, 1999; Pitchumani and Yao, 1991) applied the fractal theory to handling the effect of the composition structure and developing theoretical formulas for predicting thermal conductivity of composite materials, no theoretical formula has been published to predict the thermal conductivity of suspensions while accounting for the effect of the morphology of suspensions because of its complexity. To describe the energy transport process inside the nanofluid, a suspension system is fabricated and a steady-state process takes place: heat is transported into the system from the lefthand side and an equal amount of heat leaves the system from the righthand side. Without doubt, random motion of the suspended nanoparticle clusters intensifies the energy transport process inside the nanofluid. According to Eq. 3, the displacement per second for a nanoparticle cluster with a mean radius of gyration, r_c, is measured by the root-mean-square displacement

$$l = \sqrt{\frac{k_B T}{3\pi r_c \eta}} \tag{10}$$

when a cluster contains a single particle, $r_c = r$.

Since the radius of gyration of a cluster is larger than the radius of a single nanoparticle, the displacement of a cluster is smaller than the displacement of a particle during the same time step. For a suspension system containing n_c particle clusters, it is assumed that half of the clusters statistically move along the positive direction of the x-coordinate, and the other half move in the negative direction. By means of an approach that is similar to Bird's method (Bird et al., 1960), the transported energy flux due to the random motion of the nanoparticle clusters is given as

$$q_f = -\frac{1}{2} n_c m_c c_p l \frac{\partial T}{\partial x} \tag{11}$$

From the macroscopic point of view, this energy flux can be expressed with Fourier's law. Therefore, the thermal-conductivity component enhanced by the irregular motion of the suspended nanoparticles and/or clusters is obtained as

$$k_{\text{eff},f} = \frac{1}{2}\rho_p \phi c_p \sqrt{\frac{k_B T}{3\pi r_c \eta}} \tag{12}$$

Thus, the apparent thermal conductivity of the nanofluid is found to be

$$\frac{k_{\text{eff}}}{k_f} = \frac{k_p + 2k_f - 2\phi(k_f - k_p)}{k_p + 2k_f + \phi(k_f - k_p)} + \frac{\rho_p \phi c_p}{2k_f}\sqrt{\frac{k_B T}{3\pi r_c \eta}} \tag{13}$$

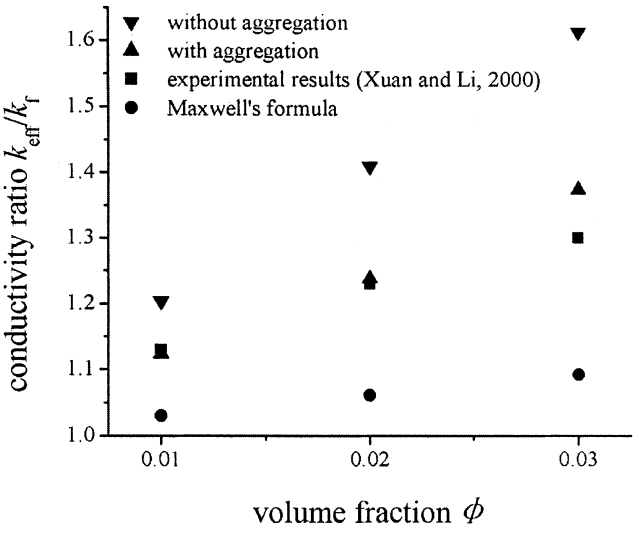

Figure 4. Thermal conductivity ratio of Cu–water nanofluid ($r = 10$ nm, $N_c = 14$).

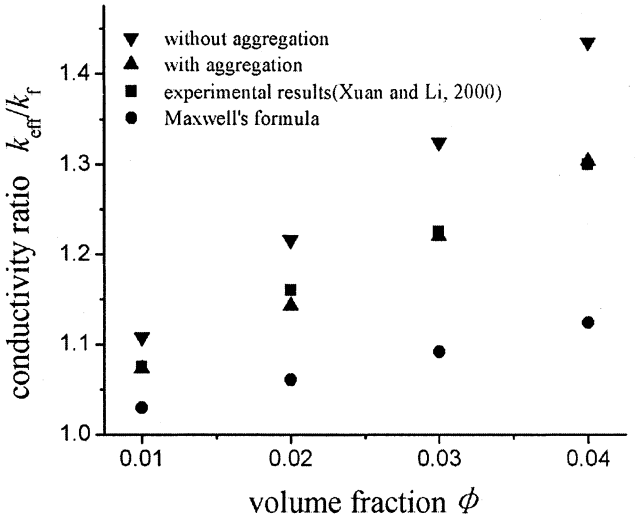

Figure 5. Thermal conductivity ratio of Cu–water nanofluid ($r = 50$ nm, $N_c = 14$).

Evidently, the thermal conductivity of the nanofluid is dependent on the viscosity of the nanofluid and the thermal conductivities of the base liquid and the solid particle as well as the density, the specific heat, and the volume fraction of the nanoparticles. It must be emphasized that the thermal conductivity of the nanofluid varies with the radius of gyration of the nanoparticle clusters or the fractal structure of the aggregates. The smaller the radius of gyration of the clusters suspended in the fluid, the larger the thermal conductivity of the nanofluid because of the fact that the smaller clusters move faster and farther in the unit time and invoke a stronger energy transport inside the nanofluid. Thus, with respect to augmentation of the thermal conductivity of the nanofluid, the contribution of the second term on the right-hand side of Eq. 13 increases.

Equation 13 provides a theoretical approach for predicting the thermal conductivity of the nanoparticle suspensions. The viscosity of the nanofluid involved in this expression can be obtained from an earlier work (Li and Xuan, 2000). Some examples for comparison between the theoretical results and the experimental ones are illustrated in Figures 4 and 5, which correspond to the case where the nanofluid temperature is equal to 296 K. From these figures, one can learn that the thermal conductivity of the nanofluid is remarkably higher than that of the original base liquid, and it will be underestimated if Maxwell's formula is used to calculate the thermal conductivity of the nanofluid. The theoretical predictions from Eq. 13 agree well with the experimental results. For the nanofluid in which no aggregation takes place and all the nanoparticles are evenly suspended, the particles are in intense random motion, which augments energy transport inside the suspension and reduces the temperature gradient inside the suspension. In such ideal cases, the highest values of the thermal conductivity are obtained (as shown by the examples of no aggregation in Figures 4 and 5). However, aggregation of the suspended nanoparticles may be inevitable, which can be determined from the TEM photographs. The aggregation process weakens the random motion of the suspended nanoparticles. According to the theory of Brownian motion, the random motion of the aggregate containing a number of nanoparticles is slower than a single nanoparticle. Once aggregation occurs and aggregates form, the intensity of the random motion of the nanoparticle clusters decreases and the function of energy transport enhancement of the nanoparticles lessens. The thermal conductivity of a nanofluid decreases as the radius of gyration of the clusters increases. By substituting r_c for the radius, r, of a single nanoparticle in order to take the effect of nanoparticle aggregation on energy-transport into account, one finds better agreement between the theoretical values and the experimental ones.

The relative contribution of the two terms to augmentation of the thermal conductivity varies mainly with the volume fraction and the radius of the suspended nanoparticles as well as the nanoparticles aggregation structure. As shown in Figure 5, for example, if $\phi = 0.03$, the contribution of the second term is 11% for the case of aggregation and 17% for the case of no aggregation; if $\phi = 0.04$, the contribution of the second term is 14% for the case of aggregation and 24% for the case of no aggregation. For the sake of energy transport enhancement, the ideal situation is that all suspended nanoparticles are evenly distributed inside the base liquid and no aggregates arise. While preparing a nanofluid, it is important to effectively suppress aggregation of the nanoparticles and to hinder formation of larger clusters. The proper preparation method makes it possible to achieve stable samples of nanofluids by changing the surface feature of nanoparticles and suppressing particle aggregation (Xuan and Li, 2000). Suitable dispersants and ultrasonic vibration can inhibit aggregation and break up clusters.

Since random Brownian motion of the suspended nanoparticles shows a strong dependence on temperature, it is expected that the thermal conductivity of a nanofluid will vary remarkably with the suspension temperature. The frequency of bombardment by the ambient fluid molecules on the nanoparticles increases as the nanofluid temperature increases, so that the frequency of random motion and the averaged velocity of the nanoparticles increase. Therefore, the energy transport contribution from the stochastic motion of the suspended nanoparticles is enhanced by increasing the temperature. Besides, the viscosity of a nanofluid decreases with an increase in the nanofluid temperature, because the viscosity of the base liquid (water) drops with increasing temperature, which also makes some contribution to random motion of nanoparticles as well as energy transport. Some theoretical predictions obtained from Eq. 13 are illustrated in Figure 6. All these curves evidently reflect such a temperature-dependent relationship. In addition, the effect of fluid temperature will become much more evident with an increase in the volume fraction of the nanoparticles and a reduction in nanoparticle sizes. It is expected that the thermal performance of a nanofluid can be further improved if it is involved in application at higher temperature levels.

Conclusions

The random motion of suspended nanoparticles is a typical Brownian motion. Such irregular motion and aggregation process of the nanoparticles have been simulated using the theory of Brownian motion and the DLA model. The fractal

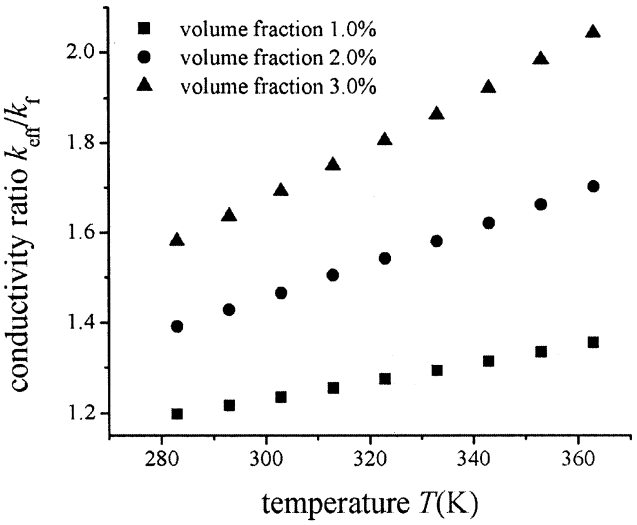

Figure 6. Effect of temperature on thermal conductivity of Cu–water nanofluid ($r = 10$ nm) without nanoparticles aggregation.

dimension is a suitable parameter to indicate the aggregation structure of nanoparticle clusters.

By considering physical properties of both the base liquid and the nanoparticles, as well as the structure of the nanoparticles, aggregates, a theoretical model has been developed to predict the thermal conductivity of nanofluids. The predictions obtained from this model are in satisfactory agreement with the experimental results, especially when the effect of nanoparticle aggregation is taken into account. The thermal conductivity of a nanofluid increases with the fluid temperature. Nanoparticle aggregation and formation of aggregates reduces the efficiency of the energy transport enhancement of the suspended nanoparticles.

Acknowledgment

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Notation

a = frictional coefficient
c_p = specific heat capacity, J/(kg·K)
D_f = the fractal dimension
$F(t)$ = random force, N
F_w = field force, N
k = thermal conductivity, W/(m·K)
m_c = mass of a nanoparticle cluster, kg
$\boldsymbol{q}$ = heat flux, W/m^2
n_c = number of nanoparticle clusters
N = number of all nanoparticles
N_c = number of the averaged nanoparticles contained in a cluster
r = radius of a nanoparticle, m
R_s = cluster radius of gyration
t = time variable, s
T = temperature, K
x = spatial variable, m

Greek letters

ϕ = volume fraction of nanoparticles
η = viscosity, kg/(s·m)
ρ = density, kg/m^3

Subscripts

c = cluster
f = liquid phase
p = nanoparticle

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