A fractal model for the effective thermal conductivity of nanoparticle suspensions*

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Abstract Extending the effective medium approximation with the fractal theory for describing nanoparticle clusters and their radius distribution, a predictive model is proposed for the effective thermal conductivity of nanoparticle suspension, combined with the consideration of size effect and surface adsorption effect of nanoparticles. The predicted effective thermal conductivity of nanoparticle suspension is consistent with experimental data in the dilute limit.

Keywords: fractal, nanoparticle suspension, surface adsorption, size effect.

Recently, the research on the effective thermal conductivity of nanoparticle suspension, which was specially termed by Choi "nanofluid" and was considered to be a novel fluid of enhanced heat transfer[1], has attracted great attention experimentally and theoretically. Compared with the normally used industrial fluid for heat transfer, the effective thermal conductivity of nanoparticle suspension can be much higher. Keblinski et al.[2] suggested that the size effect, the clustering of nanoparticles and the surface adsorption could be the major reasons of enhancement. They believed that the Brownian motion of nanoparticles contributes much less than other factors, but it can cause the clustering of nanoparticles that will indirectly enhance the effective thermal conductivity of liquid. Wang et al.[3,4] have studied experimentally the possible enhancing mechanisms of it and analyzed the effects of surface adsorption of liquid and Brownian motion of nanoparticles on the enhancement, but temporarily ignored the contribution of clustering effect. Thus, the modeling of effective thermal conductivity of nanoparticle suspension including the effect of clustering would be necessary.

Considering the concept of abnormal set, a counterexample of normal aggregation function, Mandelbrot proposed firstly the fractal theory[5]. For nanoparticles within the mesoscale limit, it can well describe the disorder and stochastic process of clustering and polarization of them. Pitchumani et al.[6] firstly used the fractal theory to study the effective thermal conductivity for unidirectional fibrous composites and obtained their fractal characters, while Yu et al.[7~9] obtained a fractal description of effective dielectric coefficient of composite material using the traditional effective medium theory and fractal theory. But, there are few reports on the use of the fractal theory in describing the clustering of nanoparticles to predict the effective thermal conductivity. In this paper, we will extend the work of Yu et al. and combine the effective medium theory and fractal theory to study the possible enhancing mechanisms of nanoparticle suspensions. We will introduce briefly the effective medium theory and the concept of fractal dimension for nanoparticle clusters, together with the consideration of particle size and surface adsorption effect, and attempt to establish a fractal model for predicting the effective thermal conductivity of liquid with nanoparticle inclusions.

1 Effective medium theory

The Maxwell-Garnett's self-consistent approximation (MG) model[10] and the Bruggeman approach[11] are the most-commonly used methods in effective medium theory to treat the effective transport coefficient of mixture and composites. The former one fits well with experimental data where the dilute and randomly distributed components are included in a homogeneous host medium and the particles are considered to be isolated in the host medium, without interactions existing among them. For the two-com-

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ponent entity, i.e. spherical-particle suspensions in a hosting liquid, the MG model[10] gives

$$\frac{k_{\mathrm{eff}}}{k_{\mathrm{f}}}=\frac{(1-\phi)(k_{\mathrm{p}}+2k_{\mathrm{f}})+3\phi k_{\mathrm{p}}}{(1-\phi)(k_{\mathrm{p}}+2k_{\mathrm{f}})+3\phi k_{\mathrm{f}}}, \quad (1)$$

where k_{eff} is the effective thermal conductivity of liquid with particle suspension, k_{f} the thermal conductivity of host medium, k_{p} the thermal conductivity of particle, and ϕ the volume fraction of particles. The MG model is applicable to the suspension with low-concentration particulate inclusions.

Bruggeman used the mean field approach to analyze the interactions among the randomly distributed particles and host liquid[11]. For a binary mixture of homogeneous spherical inclusions, the Bruggeman model gives

$$\phi\left(\frac{k_{\mathrm{p}}-k_{\mathrm{eff}}}{k_{\mathrm{p}}+2k_{\mathrm{eff}}}\right)+(1-\phi)\left(\frac{k_{\mathrm{f}}-k_{\mathrm{eff}}}{k_{\mathrm{f}}+2k_{\mathrm{eff}}}\right)=0, \quad (2)$$

and the solution of the above quadratic equation is given as

$$k_{\mathrm{eff}}=(3\phi-1)k_{\mathrm{p}}+[3(1-\phi)-1]k_{\mathrm{f}}+\sqrt{\Delta}, \quad (3)$$

$$\Delta=(3\phi-1)^2k_{\mathrm{p}}^2+[3(1-\phi)-1]^2k_{\mathrm{f}}^2+2[2+9\phi(1-\phi)]k_{\mathrm{p}}k_{\mathrm{f}}. \quad (4)$$

The Bruggeman model has no limitation on the concentration of inclusions, and can be used for particle percolation in suspensions. For a low particle concentration, Bruggeman model shows almost the same with MG model. But, as the particle concentration is sufficiently high, MG model fails to predict the experimental results, while Bruggeman model can still fit well with experimental data.

2 Fractal dimensions of clusters

Havlin et al.[12] pointed out that the radius distribution of nanoparticles and the distribution of nanoparticles in suspension have both shown some kind of self-comparability. We introduce the scaling theory to describe quantitatively the fractal system. If the volume (area, particle numbers, etc.) of fractal is $F(\varepsilon)$, then, the fractal dimension, D_{f}, can be decided through the following expression:

$$F(\varepsilon)=C\varepsilon^{D_{\mathrm{f}}}, \quad (5)$$

where ε is the unit of the scalar, C is a shape factor that is independent of ε. Electron microscopic photos of CuO clusters (the volume concentration of 50 nm CuO is 0.13%, 0.25% and 0.38%, correspondingly) suspended in deionized water are shown on the top of Fig. 1. The middle and bottom parts of Fig. 1 are the section area of each nanoparticle cluster and the calculation of their fractal dimensions. Using Eq. (5), the fractal dimension of corresponding clusters are calculated to be 1.73, 1.76 and 1.81, respectively.

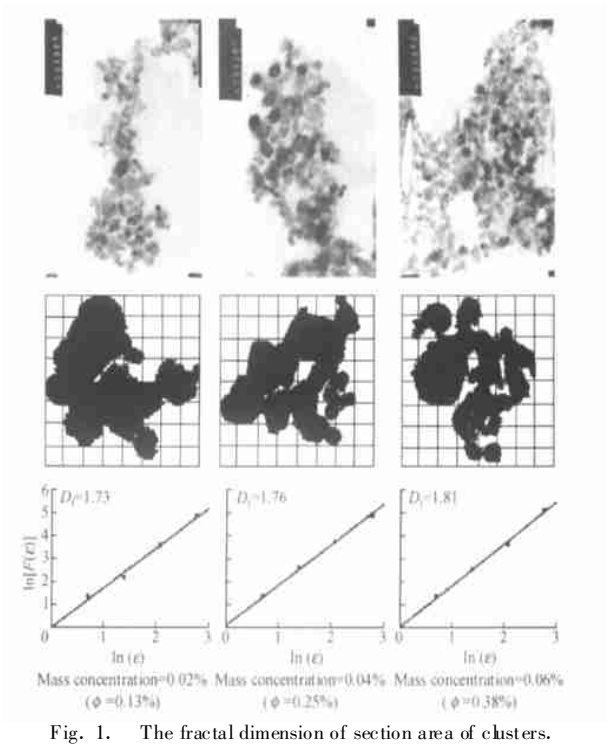

Fig. 1. The fractal dimension of section area of clusters.

3 Fractal cluster model for predicting effective thermal conductivity

The enhancement in effective thermal conductivity for nanoparticle suspension, $k_{\mathrm{eff}}/k_{\mathrm{f}}$, relates directly with the particle interaction and clustering process. The nanoparticle suspension is usually not simply composed by nanoparticles and host liquid, but is composed by host liquid and inclusions of percolation-patterned clusters. Thus, both host liquid and clusters will contribute to the effective thermal conductivity of liquid. To consider the effect of cluster distribution on establishing the effective thermal conductivity with Eq. (1), k_{p} should be replaced by the effective thermal conductivity of nanoparticle clusters, $k_{\mathrm{cl}}(r)$, which can be predicted by Bruggeman model.

3.1 Effective thermal conductivity of nanoparticle clusters, $k_{\mathrm{cl}}(r)$

Clusters of different sizes will be formed in suspension due to the interaction of nanoparticles of equal radius, a. Thus, the volume fraction of particles in clusters are bigger than that in host liquid. From the fractal theory[13], the volume fraction of particles in a

cluster with radius of r can be obtained by the following equation:

$$\phi_{cl}(r) = (r/a)^{D_f-3} \quad (6)$$

where r is the radius of nanoparticle clusters, $\phi_{cl}(r)$ is the volume fraction in clusters, and D_f is the fractal dimension. By Bruggeman approach[11], substituting $f(r)$ for ϕ into Eqs. (3) and (4), the effective thermal conductivity of cluster can be expressed as $\phi_{cl} = \phi_{cl}(r)$.

3.2 Spatial distribution of nanoparticle clusters, $n(r)$

We treat the suspension of particles with the same radii, a, and the suspension of clusters with different radius, r. It is the spatial distribution of clusters that will prominently affect the enhancement of effective thermal conductivity. The statistical method can be used to establish the spatial distribution of isolated clusters. One of these methods is the log normal distribution function, which describes the completely stochastic walk of a large amount of particles to form the disordered clusters through the short distance adherence forces. When the volume of particles can be expressed as $V = Hr^m$, in which H and m are constants of the shape factors of particles, the following log-normal distribution function can approximately be used to describe $n(r)$[14]:

$$n(r) = \frac{1}{r\sqrt{2\pi}\ln\sigma}\exp\left\{-\left[\frac{\ln(r/\bar{r})}{\sqrt{2\pi}\ln\sigma}\right]^2\right\}, \quad (7)$$

where $\bar{r}$ is the geometric mean radius, σ the standard deviation. The value of $\bar{r}$ can be substituted approximately by the norminal radii, a, and σ can take the classic value of 1.5.

3.3 Effective thermal conductivity of nanoparticle suspension

Wood et al.[15] modified the MG model with consideration of the spatial characteristic of particles. Here we further consider the effects of clustering, and obtain the effective thermal conductivity of suspension with nanoparticle inclusions. Substituting the effective thermal conductivity of clusters, $k_{cl}(r)$, and the radial distribution function, $n(r)$, into the modified MG equation, the effective thermal conductivity of nanoparticle suspension can be expressed as:

$$\frac{k_{eff}}{k_f} = \frac{(1-\phi)+3\phi\int_a^\infty \frac{k_{cl}(r)n(r)}{k_{cl}(r)+2k_f}dr}{(1-\phi)+3\phi\int_a^\infty \frac{k_f n(r)}{k_{cl}(r)+2k_f}dr}. \quad (8)$$

This equation is the proposed fractal model deduced for predicting the effective thermal conductivity of liquid with nanoparticle inclusion. The range of r for integral should be from r_1 to r_2, where r_1 and r_2 are upper and lower limit of r, respectively. The value of r_1 is usually taken as the diameter of particle, a; while r_2 is determined by the diameter and volume fraction of nanoparticles and the percolation situation of clusters whose diameters will reach even hundreds of micrometers or being comparatively ∞.

4 Consideration of particle-size effect and surface adsorption of nanoparticles

Without consideration of radiation, the heat carriers in nanoparticles include only phonons and electrons. Chen[16] established the transport regimes for these heat carriers, according to the relation between the mean free path of carriers and the length scale of nanostructures. When the mean free path of heat carriers is comparable with the size of nanoparticles, i.e. 10 ~ 100 nm, the Boltzmann equation could be applicable to the description for the heat transfer process. Hence, using the relaxation time approximation method[17], the effective thermal conductivity of nonmetallic nanoparticles can be approximated as

$$k_p = \frac{3a^*/4}{3a^*/4+1}k_b, \quad (9)$$

where k_b is the thermal conductivity of corresponding bulk material for particle, $a^* = a/l$ the nondimensional radius, and l the mean free path of phonons. For the metallic nanoparticles, the effective thermal conductivity can be achieved, provided that the Wiedemann-Franz Law still holds when the temperature is much higher than the Debye temperature. The size effect on the phonon-electron-coupling factor is also negligible within the above-mentioned regime for ranging from 10 ~ 100 nm[18]. A cubic decreasing law was found in the effective electric conductivity for particles smaller than 500 nm[19]. Thus, when the relaxation times of electron and phonon are comparable, the following equation can be used for effective thermal conductivity of metallic nanoparticles:

$$k_p = \left(\frac{2a}{5\cdot 10^{-6}}\right)^3 k_b. \quad (10)$$

Now, we take insights into surface adsorption. The adsorption of liquid molecules on the particle surface is thought to be a monolayer one. The way of molecule allocation on the surface is commonly considered to be a hexagonal closed-packed style. From the

Langmuir formula of monolayer adsorption of molecules, the thickness of the adsorption layer can be expressed as[20]

$$t = \frac{1}{\sqrt{3}}\left(\frac{4M}{\rho_f N_A}\right)^{1/3}, \quad (11)$$

where M is the molecular weight of liquid, ρ_f the density of liquid, and N_A Avogadro constant (6.023×10^{23}/mol). Since the monolayer always occurs in conjunction with the particle sphere, they are completely correlated, and hence, the effective thermal conductivity of the nanoparticle can be considered to be the total thermal conductivity of these two substances[15]:

$$k_{cp} = k_{ad}\frac{(k_p+2k_{ad})+2A^3(k_p-k_{ad})}{(k_p+2k_{ad})-A^3(k_p-k_{ad})}, \quad (12)$$

where $A=1-t/(t+a)$, k_{ad} is the effective thermal conductivity of the adsorption layer. With the consideration of surface adsorption, we should substitute $(a+t)$, $[(a+t)/a]^3\phi$ and kcp for a, ϕ and k_p, respectively, in Eqs. (2)~(10). The value of k_{ad} is hard to be predicted, but from Eq. (12), we assume that k_{ad} can take k_{cp} as the first approximation, and thus the calculated results will stand for the upper bound of enhancement for effective thermal conductivity of liquid with nanoparticle inclusions.

5 Discussion

In the classical effective medium theories, neither MG model[10] nor the Bruggeman model[11] considers the interaction between particles in host medium. The three-component Core-Shell-Medium (CSM) model[21] deduced from the MG approximation has considered the adsorption process on the particle surface. The Rayleigh model[22] did not concern the effect of particle interaction, but for particles of small radius, its accuracy is higher than MG model. The Cichocki-Felderhof (CF) model[23] came from statistical method and considered the interaction between particles of the same radius. The Monecke model[24] discarded the physical topology technique of effective medium theory, deduced on the assumption that the effective thermal conductivity equals an interpolation between the extreme limits of its components. Using the data listed in Table 1, we compare these models with experimental results for suspension of CuO nanoparticles with norminal diameter of 50 nm in deionized water[25] as listed in Table 2. All these models function the same in dilute limit, yet neither of them nor our previous paper that considers the clustering effect[4] can explain well with our experimental data[25] with estimated uncertainty of k_{eff} to be $\pm2.9\%$[25].

Table 1. Data for calculation

Copper oxide		Deionized water	
Average radius, a	25 nm	Thickness of adsorption monolayer, t	2.8 nm
Mean free path of phonons, l	14 nm		
Density, ρ_p	6310 kg/m^3	Density, ρ_f	996 kg/m^3
Thermal conductivity, k_p	32.9 W/m/K	Thermal conductivity, k_f	0.613 W/m/K

Table 2. Comparison of the calculated value of k_{eff}/k_f using various models

Particle volume fraction (%)	Bruggeman model[11]	CSM model[21]	Rayleigh model[22]	CF model[23]	Monecke model[24]	Experimental results[25]
0.1	1.00262	1.00192	1.00262	1.00266	1.00262	1.0982
0.2	1.00526	1.00386	1.00524	1.00539	1.00525	1.1252
0.3	1.00791	1.00582	1.00787	1.0082	1.00788	1.13984
0.4	1.01057	1.00781	1.01051	1.01108	1.01051	1.16996
0.5	1.01324	1.00982	1.01314	1.01404	1.01316	1.11238
0.6	1.01593	1.01185	1.01579	1.01708	1.01581	1.10531

Taking suspension of CuO nanoparticles (50 nm) in deionized water as an example, the effective thermal conductivity of it can be calculated from the proposed fractal model, in which the dimension of cluster can correspondingly be taken from Fig. 1, while r_1 and r_2 are taken as 5 nm and 500 μm, respectively. The calculated result is compared with our experimental result[25] in Fig. 2. It can be seen that the modified fractal model fits well with the experimental data when the particle concentration, ϕ, is less than 0.5%, which approaches the measured results better than our previous work[4], and that the spatial distribution of clusters should be carefully considered. The proposed fractal model assumes as usual that the diameters of these spherical nanoparticles are the same. We will further investigate the other factors such as

size effect, radius distribution of cluster, shape factor of nanoparticle, etc. In short, further research work would be needed to refine the model we proposed here, especially for suspension of metallic nanoparticles.

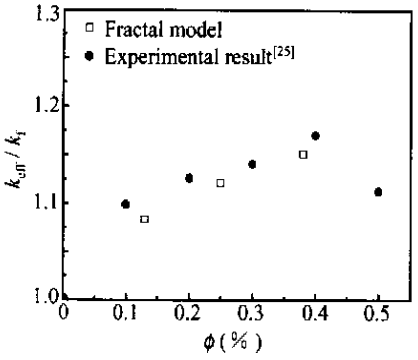

Fig. 2. Comparison of proposed fractal model with experimental data for CuO/deionized water.

6 Conclusions

Based on the effective medium theory, we proposed here a fractal model for predicting the effective thermal conductivity of liquid with a dilute suspension of nonmetallic nanoparticles. It involves the application and improvement of the effective medium theory. The calculated result shows that the fractal model can predict well the trend of effective thermal conductivity of nanoparticle suspension in the dilute limit.

The calculated result also shows that the predictive calculation of effective thermal conductivity is complicated. Further work that will better describe the spatial distribution of nanoparticle cluster would be needed for the development and research of new engineering fluids.

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