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A Novel Statistical Clustering Model for Predicting Thermal Conductivity of Nanofluid

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Abstract An analytical method is proposed to predict the thermal conductivity of nanofluids by use of the macroscopic statistical characteristics of particle clustering suspensions. The algorithm is much simpler and more convenient than the fractal model method suggested and reported before. It is shown with numerical calculation and discussion that reliable predictions of the thermal conductivity for a nanofluid can be reached with the method presented in this paper. The physical meaning and practical prospects in the research and development for screening and optimizing nanofluids as new advanced working fluids are presented.

Keywords Nanofluid · Particle clustering · Physical–mathematical model · Thermal conductivity

1 Introduction

In the past 25 years, research progress in micro-scale thermophysics not only advanced a deep understanding in matter science, such as surface physics, agglomerative state, phase change, and phase interfacial transport phenomena, but also promoted technology innovation for equipment miniaturization, and thus, provided new opportunities for researching new types of working liquids and their thermal processes. Maxwell's classical theory of "effective medium" [1], reported in 1873, indicated that suspended solid particles will improve the effective thermal conductivity of a liquid. Since then, many researchers have conducted investigations theoretically and/or experimentally in this area. However, mm/μm-sized solid particles may settle out of the fluid, and hence, be deposited on the heating/cooling surface. The terminology "nanofluid" was

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introduced by Choi in 1995 [2] for a liquid with nm-sized particles/fibers suspended; research included thermophysical properties reviewed in [3], such as thermal conductivity [2–6], thermal diffusivity [3,5,6], specific heat capacity [7], viscosity [8], etc.; and the related transport phenomena [9,10] have been then widely developed in the world. It is recognized that metal oxide nanoparticles of low concentration by volume, $\phi_p \leq 1\%$, can significantly increase the thermal conductivity to a level much higher than that predicted by the theory of the effective media approximation proposed by Maxwell [1]. This will enhance the potential ability of heat transmission and phase change heat retention.

The surface adsorption of suspended particles, together with the growth of clusters and their distribution are typical nonequilibrium processes. The state of the art in micro-fabrication can meet the objective to prepare different nanofluids, and the stability of suspended nanoparticles may be controlled. The influences of Brownian motion, surface adsorption, and particle clustering have been discussed [3–6,9,10]. The velocity of random Brownian motion is small, but it creates opportunities for the particles to be clustered or agglomerated. Surface adsorption will help avoid direct contact in particle clustering. The particles' clustering increases the local concentration of nanoparticles. Due to the lack of data credibility as a whole, predictive calculations for screening and optimizing nanofluid performance have become very difficult and questionable.

Scanning electron microscope (SEM) photographs [3,6] of a nanofluid containing 50 nm-diameter CuO and de-ionized water or 25 nm-diameter SiO_2 and de-ionized water show that the clustering of particles is characterized as fractals. The fractal dimension for different volumetric concentrations of particles, $\phi_{p,}$ can be evaluated from the SEM photo. So, a fractal model has been established to obtain the thermal conductivity of nanofluids[6]. However, actual measurements are required to get the fractal dimensions and complex calculations may prevent that method from practical application. In the present article, a new rational macroscopic calculation model is proposed for evaluating simply and conveniently the thermal conductivity of a specified nanofluid.

2 General Considerations

Surface adsorption on suspended nm-size particles forms generally a single-molecular layer, the thickness of which, t, can be calculated from the well-known Langmuir formula:

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

where M_f is the molar mass of the liquid, ρ_f is the density of the liquid, and N_A is Avogadro's number which equals 6.023×10^{23}/mol. The thickness of the adsorption layer, t, is determined by the property of the liquid, but the densification of the adsorption layer affects further the compatibility of the particle surface to the surrounding liquid.

Since the suspended particles appear always together with surface adsorption layers, the particle and its adsorption layer can be regarded as an equivalent spherical "clustering element" with a radius of $(a + t)$, where a is the radius of a particle. The volumetric concentration of the particle in the element will be $\phi_0 = \frac{a^3}{(a+t)^3}$, while for the liquid phase in the element it will be $(1 - \phi_0)$.

When the elements are aggregated together to form a cluster with an equivalent radius of r, the concentration of particles becomes higher locally, and its distribution would be inhomogeneous. Suppose the elements in the cluster are aggregated in a cubical array, the volumetric concentration of the solid particles is $\frac{4}{3}\pi r^3/[2(a+t)]^3 = 0.524$, which indicates the porosity or spatial proportion ε of the new additional gap between adjacent aggregated elements in the whole cluster, i.e., ε = (1 – 0.524) = 0.476. As a result, the free liquid will be absorbed into the cluster. Thus, the volumetric concentration of the solid particles in the cluster will be

$$(\phi_{\mathrm{p}})_{\mathrm{cl}} = 0.524\ \phi_0. \tag{2}$$

Both the liquid and solid particles are incompressible under moderate pressure. When the elements are aggregated in an ideal cubical array, the structural characteristic of a cluster, $(\phi_{\mathrm{p}})_{\mathrm{cl},}$ is independent of the particle concentration ϕ_{p} in the nanofluid. However, in fact, the possibility of clustering increases with ϕ_{p}, so the particles packed in a cluster may be underestimated and the free liquid between aggregated elements will be partially forced out of the cluster.

Consider the possible different kinds of aggregation, the simple cubic array, with $(\phi_{\mathrm{p}})_{\mathrm{cl}}$= 0.524, will be the loosest one. For the body-center cubical array, $(\phi_{\mathrm{p}})_{\mathrm{cl}}$= 0.65; and for the face-center cubical array, $(\phi_{\mathrm{p}})_{\mathrm{cl}}$= 0.74. We take $(\phi_{\mathrm{p}})_{\mathrm{cl}}$= 0.63 as the mean value instead of the value 0.524 in Eq. 2 and, correspondingly, ε = 0.37 in the following analysis.

3 Macroscopic Characteristics of Clusters in Nanofluids

Denote the statistically average nominal radius of the cluster as $\overline{r}_{\mathrm{cl}}$ and the average density as $\overline{\rho}_{\mathrm{cl}}$, or

$$\overline{\rho}_{\mathrm{cl}} = \frac{\int_0^\infty \rho_{\mathrm{cl}} \upsilon_{\mathrm{cl}}(r) n_{\mathrm{cl}}(r)\mathrm{d}r}{\int_0^\infty \upsilon_{\mathrm{cl}}(r) n_{\mathrm{cl}}(r)\mathrm{d}r} \tag{3}$$

where r is the cluster equivalent radius, υ_{cl} is the cluster specific volume, and n_{cl} is the cluster number density. Both the cluster number density and the particle number density follow the logarithmic normal distribution [11]:

$$n(r) = \frac{1}{\sqrt{2\pi}\ln\sigma} \exp\left\{-\left(\frac{\ln r/\overline{r}}{\sqrt{2}\ln\sigma}\right)^2\right\} \tag{4}$$

where the RMS deviation σ generally takes the classical value of 1.5 and $\overline{r}$ equals the statistical average of r, that is, a for a particle and $\overline{r}_{\mathrm{cl}}$ for a cluster.

The clustering of particles represents a self-sustained macroscopic phenomenon. According to Eq. 2, ϕ_0 is determined by the nominal spherical radius, a, of the particle and its adsorption layer thickness, t. ϕ_0 is independent of the cluster size, so $(\phi_p)_{cl}$ can be considered as a statistically average macroscopic quantity $(\overline{\phi}_p)_{cl}$, and ρ_{cl} can be expressed as

$$\rho_{cl} = (\overline{\phi}_p)_{cl}\rho_p + [1 - (\overline{\phi}_p)_{cl}]\rho_f$$

where ρ_p and ρ_f are the density of the particle and liquid, respectively. Then, Eq. 3 becomes

$$\overline{\rho}_{cl} = (\overline{\phi}_p)_{cl}\rho_p + [1 - (\overline{\phi})_{cl}\rho_f] \tag{5}$$

$\overline{\rho}_{cl}$ is the macroscopic statistically average density, or

$$(\overline{\phi}_p)_{cl} = \frac{\overline{\rho}_{cl} - \rho_f}{\rho_p - \rho_f} \tag{6}$$

As long as there is no chemical change in the nanofluid, both the mass of particles and the mass of the liquid would, respectively, remain unchanged before and after clustering. The partial density of the nanoparticles in the nanofluid before clustering is $\rho_p\phi_p$, and the density of the nanofluid is $\rho_{nf} = \phi_p\rho_p + (1-\phi_p)\rho_f$. After clustering, the cluster density is $\overline{\rho}_{cl}\overline{\phi}_{cl}$, and $\rho_{nf} = \phi_{cl}\overline{\rho}_{cl} + (1-\phi_{cl})\rho_f$ for the nanofluid. We have

$$\phi_p\rho_p + (1-\phi_p)\rho_f = \phi_{cl}\overline{\rho}_{cl} + (1-\phi_{cl})\rho_f$$

or,

$$\frac{\phi_{cl}}{\phi_p} = \frac{\rho_p - \rho_f}{\overline{\rho}_{cl} - \rho_f} \tag{7}$$

From Eqs. 6 and 7, the following conclusion is reached:

$$\frac{\overline{\phi}_{cl}}{\phi_p} = \frac{1}{(\overline{\phi}_p)_{cl}} \tag{8}$$

In fact,

$$\frac{\overline{\phi}_{cl}}{\phi_p} = \frac{\int_0^\infty \upsilon_{cl} n(r)\mathrm{d}r}{\int_0^\infty \upsilon_p n(r)\mathrm{d}r} \tag{9}$$

where n is the number density, υ_{cl} is the volume of a cluster, and $\upsilon_p = \frac{4}{3}\pi a^3$. The particle nominal radius is a, and the number density of particles and clusters both follows the logarithmic normal distribution in Eqs. 4 and 7 can be simplified as

$$\frac{\overline{\phi}_{\mathrm{cl}}}{\phi_{\mathrm{p}}} = \frac{1}{\upsilon_{\mathrm{p}}} \frac{\int_0^{\infty} \upsilon_{\mathrm{cl}} n(r)\mathrm{d}r}{\int_0^{\infty} n(r)\mathrm{d}r} = \frac{\overline{\upsilon}_{\mathrm{cl}}}{\upsilon_{\mathrm{p}}}$$

or,

$$\frac{\overline{\phi}_{\mathrm{cl}}}{\phi_{\mathrm{p}}} = \left(\frac{\overline{r}_{\mathrm{cl}}}{a}\right)^3 \tag{10}$$

Equations 5, 6, 8, and 10 indicate the macroscopic statistically average quantities of the cluster parameters.

4 Thermal Conductivity of Low Concentration Nanofluids

Bruggeman [12] proposed a formula for predicting the thermal conductivity λ_{em} of a liquid with solid particle suspensions from the effective media approximation (EMA) theory:

$$\left(\frac{\lambda_{\mathrm{p}} - \lambda_{\mathrm{em}}}{\lambda_{\mathrm{p}} - \lambda_{\mathrm{f}}}\right)\left(\frac{\lambda_{\mathrm{f}}}{\lambda_{\mathrm{em}}}\right)^{1/3} = 1 - \phi \tag{11}$$

It can be rewritten as

$$\frac{\lambda_{\mathrm{p}}}{\lambda_{\mathrm{f}}} - X = (1 - \phi)\left(\frac{\lambda_{\mathrm{p}}}{\lambda_{\mathrm{f}}} - 1\right) X^{1/3} \tag{12}$$

Thus, the enhancement ratio in the thermal conductivity of the suspending liquid caused by the existence of solid particles can be calculated, or the enhancement ratio in the thermal conductivity of the effective media, $X_{\mathrm{em}} = \frac{\lambda_{\mathrm{em}}}{\lambda_{\mathrm{f}}}$. Once the volumetric concentration of the particles, ϕ, approaches 0, X_{em} will approach 1.

Equation 12 can be rewritten as

$$\frac{\lambda_{\mathrm{p}}}{\lambda_{\mathrm{f}}} - \overline{X}_{\mathrm{cl}} = [1 - (\overline{\phi}_{\mathrm{p}})_{\mathrm{cl}}]\left(\frac{\lambda_{\mathrm{p}}}{\lambda_{\mathrm{f}}} - 1\right) \overline{X}_{\mathrm{cl}}^{1/3} \tag{13}$$

The enhancement ratio, X_{cl}, for the cluster's thermal conductivity can then be calculated. We can rewrite Eq. 12 as

$$\frac{\overline{\lambda}_{\mathrm{cl}}}{\lambda_{\mathrm{f}}} - X_{\mathrm{nf}} = (1 - \overline{\phi}_{\mathrm{cl}})\left(\frac{\lambda_{\mathrm{cl}}}{\lambda_{\mathrm{f}}}\right) X_{\mathrm{nf}}^{1/3} \tag{14}$$

Thus, the enhancement ratio, $X_{\mathrm{nf}} = \lambda_{\mathrm{nf}}/\lambda_{\mathrm{f}}$, can be finally predicted for the nanofluid.

As a numerical example, we calculated the thermal conductivity of a nanofluid containing CuO particles ($a = 25$ nm) suspended in de-ionized water, to compare with the predicted results by the fractal model [6], which have been checked against the experimental data. The basic data of nm-sized CuO particles and de-ionized water

are the same as in [6], i.e., $\rho_p = 6310\,\mathrm{kg \cdot m^{-3}}$and $\rho_f = 996\,\mathrm{kg \cdot m^{-3}}$; $\lambda_p = 32.9\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and $\lambda_f = 0.613\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. As a transport property, the test data on thermal conductivity, λ, should have a higher uncertainty than the density, ρ, an equilibrium property. The thickness of the adsorptive water layer is $t = 2.85\,\mathrm{nm}$ from Eq. 1. The radius of the nanoparticle clustering element is $(a + t) = 27.85\,\mathrm{nm}$, and the corresponding volume component of the particles, $\phi_0 = (\frac{a}{a+t})^3 = 0.72$. According to Eq. 2, using a constant value of 0.63 instead of 0.524, the volumetric concentration of the solid particles will be $(\overline{\phi}_p)_{cl} = 0.38$, which is independent of the particle volume component, ϕ_p, in the nanofluid. Using Eq. 8, $\overline{\phi}_{cl} = 0.0026$ for $\phi_p = 0.001$ will increase to $\overline{\phi}_{cl} = 0.026$ for $\phi_p = 0.01$. It is easy to find the mean value X_{cl} for a cluster from Eq. 13 by cut-and-try calculations, and then X_{nf} from Eq. 14. The predicted results are summarized and compared with those predicted by the fractal method [6] in Fig. 1. The experimental data points and the predicted value, $X_{em,}$ directly from Eq. 11 are included also for reference.

The analytical method proposed here is rational, without any special assumptions or hypotheses, and the physical concepts are sound. However, it is obvious from Fig. 1 that the results are under-predicted, systematically lower then those from the fractal method. The possible deviations have been explained partly in discussing Eq. 2. The macroscopic statistical model would be actually static, and the effect of dynamic factors, such as the mutual diffusion and dispersion are simplified. Fortunately, as shown in Fig. 1, increasing ϕ_p from 0.1% to 1%, the predicted thermal conductivities differ from the results of the fractal method [6] within 8 %. Compared to the complexity of the random clustering process, the calculation by the present method is much easier, and a conservative prediction of the thermal conductivity uncertanty is less than 10 %. It seems clear that the proposed method in this paper may be useful for searching, screening, and optimizing nanofluids.

In practice, a small amount of dispersant agent added to the base liquid may prevent the particles from aggregation, and thus, may help to prepare a stable nanofluid with a more uniform distribution. In such a case, ρ_f and λ_f should be, respectively, the density and thermal conductivity of the base liquid (solvent) and the dispersant agent as a solute, and in Eq. 1 M_f should be the reduced molar mass of the solution.

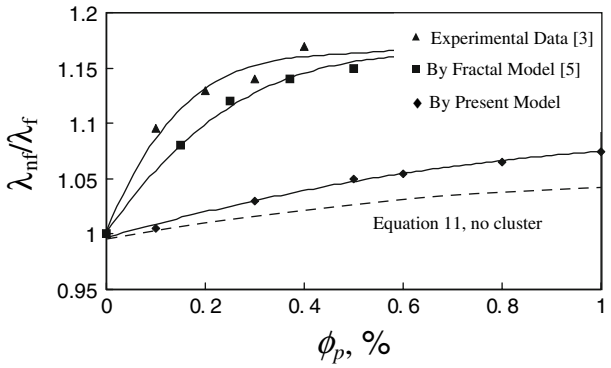

Fig. 1 Thermal conductivity of nanofluid: 50 nm CuO–Water

The high molar mass of the dispersant agent will increase the surface adsorption layer thickness, t, in Eq. 1, and hence, decrease $(\overline{\phi}_{\mathrm{p}})_{\mathrm{cl}}$. Meanwhile, $\overline{\phi}_{\mathrm{cl}}$ is enhanced to some extent, but it has little effect on λ_{nf} of a dilute nanofluid. As a result, $\lambda_{\mathrm{nf}}/\lambda_{\mathrm{f}}$ decreases.

5 Concluding Remarks

Particles suspended in a fluid will aggregate naturally into clusters under the control of the Brownian motive force and the Van der Waals force against gravity. In the present article, a statistical clustering model is proposed to determine the macroscopic characteristics of clusters, and then, the thermal conductivity of a nanofluid can be successfully estimated according to the existing effective media approximation theory. The thermal conductivities corresponding to different particle concentrations, ϕ_{p}, were calculated as a numerical example for a nanofluid with CuO particles (50 nm diameter) suspended in de-ionized water.

As discussed here, the proposed statistical model is sound in physical concepts and potentially useful as an effective tool for screening and optimizing nanofluids as advanced working fluids.

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