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Research Paper

Choice of appropriate aggregation radius for the descriptions of different properties of the nanofluids

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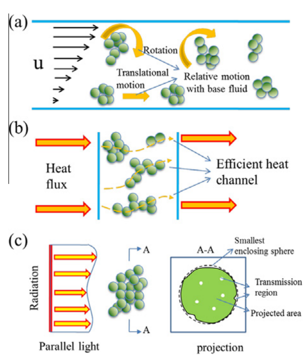
HIGHLIGHTS

- Three equivalent radii for nanoparticle aggregates in nanofluid were compared.
- Relations among three aggregation radii constructed based on aggregation algorithm.
- Appropriate aggregation radius needed for describing different properties of the nanofliud.
- Criterion for the choice of different aggregation radii was proposed.

GRAPHICAL ABSTRACT

Our experimental results show that hydrodynamic radius, gyration radius and smallest sphere enclosing radius have acceptable accuracies when predicting viscosity, thermal conductivity and absorption coefficient, respectively. Based on these findings, in the last part, criterion for the choice of three aggregation radii in predicting various physical properties of nanofluid, has been elaborated.



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ABSTRACT

Nanofluids with suspensions containing nanoparticles, have been considered to have great potential in the application of energy conversion, chemical technology or heat transfer enhancement. Due to the high surface energy, nanoparticles in nanofluid tend to form large secondary aggregates. The aggregation and the size increase could lead to significant change in various physical properties of the suspension. It is well known that many kinds of equivalent radii can be potentially employed in the description of the particle aggregates, such as hydrodynamic radius (R_h), gyration radius (R_g) and smallest sphere enclosing radius (R_s) etc. However, in most of previous study, only hydrodynamic radius was used to study the effect of the aggregation on the properties of the nanofluids. Systematic study on the appropriate choice of the equivalent radii for the description of the different properties of the nanofluids, is rare. In this study, the three representative equivalent radii of nanoparticle aggregates, R_h, R_g and R_s, were studied. It was found that for both diffusion limited cluster–cluster aggregation (DLCA) and reaction limited cluster–cluster aggregation (RLCA), the general sequence is $R_h < R_g < R_s$. The three equivalent radii were correlated with each other by Monte Carlo method using an off-lattice cluster–cluster aggregation algorithm. The relationship is useful because hydrodynamic radius can be obtained experimentally from light scattering technique, while the other two are difficult to obtain experimentally. In our study, based on hydrodynamic radius obtained by DLS method, the other two equivalent radii were successfully obtained based on the proposed relationship. By comparing the experimental results with theoretical prediction, it was found that R_h, R_g and R_s showed the better accuracy when predicting viscosity, thermal conductivity

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and absorption coefficient, respectively. Based on these findings, in the last part, we propose a criterion for the choice of appropriate aggregation radii in predicting different physical properties of nanofluid. Our study is expected to provide a valuable guidance for the study of the effect of particle aggregation on the various properties of the nanofluids.

1. Introduction

In the absence of an anti-agglomeration agent, sometimes even in the presence of this agent, nanoscale particles in colloid suspension will generally form large secondary aggregates due to their high surface energy. The randomness and isotropy (for non-magnetic nanofluids) of aggregation process always cause aggregates exhibiting fractal structures [1–3]. Fractal aggregates are characterized by a density decreasing with increasing number of particles in the cluster. Two limiting aggregation regimes have been identified. In diffusion limited cluster–cluster aggregation (DLCA), in which every collision between two clusters or particles results in the formation of a new cluster which generally have fractal dimension of around 1.8 [4]. In reaction limited cluster–cluster aggregation (RLCA), only a small fraction of collisions leads to the formation of new cluster. This kind of aggregates generally has a dimension of ca. 2.1 [5]. Due to the resulting complex structure, it is difficult to describe the aggregate size by a single parameter such as radius.

Typically, there are three kinds of equivalent diameters employed to describe the aggregate size, namely, hydrodynamic radius (R_h), gyration radius (R_g) and smallest sphere enclosing radius (R_s) [3,6,7]. The hydrodynamic radius of aggregate R_h is defined as the size of the equivalent sphere that moves (such as sedimentation and Brownian motion) with the same velocity as the aggregate in a fluid, which depends on the geometrical arrangement of particles. In mathematical sense, hydrodynamic radius satisfies

$$D = \frac{k_B T}{6\pi\eta \times (2R_h)} \tag{1}$$

where the Stokes–Einstein relation has been used. D is diffusion coefficient of aggregate or nanoparticle, k_B is the Boltzmann constant, T is thermodynamic temperature and η is dynamic viscosity of base fluid. Kirkwood–Riseman theory, a method to obtain the force of individual particle, has been used in some previous work to derive an analytical formula for the evolution of the hydrodynamic radius [3,8]. By introducing a simplified approach based on the calculation of the force acting on the average particle in a cluster, Kirkwood–Riseman theory requiring only the knowledge of all the interparticle distances in the cluster. Actually, the needed information can be easily obtained by Monte Carlo method [9,10].

Gyration radius R_g is determined by only the aggregation structure, i.e. the relative location of every nanoparticle in an aggregate, which can be shown as

$$R_g = \left(\sum_{i=1}^{N} \frac{r_i^2}{N}\right)^{1/2} = \left[\sum_{i=1}^{N} \frac{(x_i - x_G)^2 + (y_i - y_G)^2 + (z_i - z_G)^2}{N}\right]^{1/2} \tag{2}$$

where N is the number of particles in an aggregate (also called dimensionless mass), r_i the distance between ith particle and center of gravity of aggregation, point ($x_G\ y_G\ z_G$) is the center of gravity of an aggregate. Obviously, Gyration radius indicates the compactness of an aggregate. Correlating gyration radius and fractal dimension, we have

$$N = k_f (R_g/R_p)^{D_f} \tag{3}$$

where k_f and D_f are the fractal prefactor and fractal dimension, respectively R_p is the primary particle radius. The parameters k_f and D_f can be obtained conveniently by Monte Carlo simulations. Filippov has obtained the values as $k_f = 1.117$ and 0.94, while $D_f = 1.85$ and 2.05, in DLCA and RLCA, respectively [4,5].

The smallest sphere enclosing radius indicates the radius of smallest spherical space containing the aggregate. Note that it is meaningless to define smallest sphere enclosing radius for magnetic nanofluid in magnetic field due to the chain-like aggregation structure. The above mentioned three different equivalent diameters for the description of the same aggregate are schematically shown in Fig. 1. Based on above discussion, one can see that these diameters describe aggregates from different views, thus their values and ranges of application should be different.

Both experimental and theoretical studies have shown that aggregate size has a significant effect on thermal conductivity, heat transfer efficiency, optical properties and rheological properties of nanofluid [11–15]. However, there is no widely accepted criterion for choosing which equivalent radius when one tries to describe the thermophysical or optical properties of nanofluid. On the other hand, more convenient and accurate method to obtain the equivalent radii other than Monte Carlo simulation is also preferred. As is known, Monte Carlo method is time consuming and need many approximations when employed, which is an obvious weakness for practical application. Multiangle dynamic light scattering (DLS) has been proven to be a powerful tool for the experimental investigation of particle aggregation [6,7,15]. In DLS method, coherent light is launched into the nanofluid. The particles or aggregates scatter the light and some of scattering light would encounter and form interference patterns. By recording and analyzing the changing of interference patterns, one can obtain the diffusion coefficient. Combined with Eq. (1), hydrodynamic radius of aggregates would be obtained. Although hydrodynamic radius can be measured experimentally, the packing structure of the aggregates is still not available. Based on Fig. 1, if the other two equivalent radii, R_g and R_s can be also obtained, understanding of the structure of the aggregates could be possible. However, R_g and R_s is often difficult to be obtained experimentally. One alternative solution is to obtain these two equivalent radii by finding the underlying relationship between the three equivalent radii. This is indeed the target of our present work.

In this study, Firstly, we introduce a simple model to establish the relationship of the three equivalent radii. As hydrodynamic radius can be measured rapidly and accurately, efficient conversion from hydrodynamic radius to gyration radius or/and smallest sphere enclosing radius becomes significant and useful. In order to find the relationship, Kirkwood–Riseman theory and some empirical formula have been employed in our study. Secondly, we try to propose a criterion as to how to choose a proper equivalent radius when discussing different properties of nanofluids, such as thermal conductivity, absorption coefficient etc. We calculate those thermophysical properties by corresponding equivalent radius of aggregates in nanofluid and meanwhile, obtain those parameters experimentally. By comparing and discussing the experimental and predicted values, we suggested the ranges of application for hydrodynamic radius, gyration radius and smallest sphere enclosing radius, respectively.