International Journal of Heat and Mass Transfer 127 (2018) 1138–1146

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

# Investigation of the aggregation morphology of nanoparticle on the thermal conductivity of nanofluid by molecular dynamics simulations

Ruijin Wang *, Sheng Qian, Zhiqi Zhang

*School of Mechanical Engineering, Hangzhou Dianzi Unversity, Hangzhou 310018, PR China*

ARTICLE INFO

*Article history:*
Received 5 July 2018
Received in revised form 18 August 2018
Accepted 24 August 2018

*Keywords:*
Nanofluid
Equilibrium molecular dynamics
Aggregation morphology
Fractal dimension
Effective thermal conductivity (ETC)

ABSTRACT

Nanofluid can enhance heat transfer due to the suspending nanoparticles. The mechanism of heat transportation by nanoparticles remains unclear so far. Aggregation of nanoparticles, one of the important mechanisms to elevate the thermal conductivity of nanofluid, was proved by not a few researches. However, the aggregation morphology of nanoparticles evaluated by fractal dimension will greatly influence the thermal conductivity of nanofluid. In this paper, equilibrium molecular dynamics simulations were carried out to calculate the thermal conductivity via Green-Kubo formula. In contemporary, fractal dimensions of the aggregations with various morphologies were obtained by Schmidt-Ott equation. Comparisons of the fractal dimension and thermal conductivity of the nanofluid with same volume fraction show us that, lower fractal dimension can deduce greater thermal conductivity. In addition, the difference of loose and compact aggregation can be read out of the pair correlation function near nanoparticles. And the solvent atoms in nanolayer are mobilized and dynamically balanced. This is helpful for us to understand the influence of aggregation morphology of nanoparticles on the thermal conductivity of nanofluid.



## 1. Introduction

Great interests of many researchers were aroused in recent two decades due to the great heat transfer enhancement of nanofluid as a heat transfer medium. Choi [1] found in 1995 that, adding nanoparticles in liquid can greatly improve the heat transfer performance of liquid, especially at very low volume fraction of nanoparticle (normally less than 0.01%). Minkowycz [2] analyzed how the nanoparticle improve the heat transfer enhancement. So-called "nanofluid" refers to the liquid suspending homogeneously nanoparticles. Effective thermal conductivity (ETC) was normally used to evaluate the heat transfer performance of nanofluid. Primary ETC model was established by Maxwell [3] based on the effective medium theory, considering the nanoparticles are static and homogeneous. Hereafter, some ETC models taking nanoparticle shape, Brownian motion of nanoparticles, nanolayer around the nanoparticle and nanoparticle aggregation into accounts were established by Hamilton-Crosser [4], Xuan et al. [5], Yu and Choi [6], Prasher [7], respectively. However, all above models deduced from Maxwell model are based on the hypothesizes, that is, all nanoparticles are static and homogeneous dispersion in liquid. Pabst [8] concluded after the analysis on the published experimental results from the perspective of micromechanics that, the Wiener bounds could be a key criterion to verdict the reasonability of the research approaches and results of ETC, if the nanoparticles are static and homogeneous dispersion. Unfortunately, contradictories and inconsistencies among experimental results, theoretical results and numerical results were not uncommon because the micromechanism of the heat transfer enhancement of nanofluid remains unclear so far. Xue et al. [9] concluded by molecular dynamics simulations that, the nanolayer around the nanoparticle has no influence on the heat transportation. In addition, the nanolayer could decrease the thermal conductivity due to the interfacial thermal resistance [9]. Evans [10] theoretically investigated and Azimi [11] numerically simulated by molecular dynamics, they found the influence of Brownian motion of nanoparticle on the thermal conductivity is limited and can be omitted. The comprehensive analysis on a series of experimental results by Bianco et al. [12] shows that, Brownian motion, nanolayer and near field radiation are not the crucial reasons to elevate the thermal conductivity of nanofluid, the intrinsic reason is right nanoparticle aggregation which can be predicted by effective medium theory.

Aggregations or clusters of nanoparticles can be easily observed in experiments, and effect the thermal conductivity greatly. A new model taking the aggregation into account was derived from

* Corresponding author.
*E-mail address:* wangrj@hdu.edu.cn (R. Wang).

https://doi.org/10.1016/j.ijheatmasstransfer.2018.08.117
0017-9310/

Bruggeman model and Maxwell-Garnett by Evans et al. [13], and verified by direct simulation Monte Carlo method. Feng et al. [14] established a new model involving aggregation of nanoparticles, and showed that, the smaller the nanoparticles are, the more aggregations, and the greater the ETC. Sedighi [15] investigated the ETC by molecular dynamics and concluded that, aggregation of nanoparticles can improve the ETC of nanofluid at a fixed nanoparticles concentration. The investigation of Hong [16] showed us that, gelation aggregation can increase ETC greatly. The most interesting thing is that, the ETC of magnetic fluid with $Fe_3O_4$ nanoparticles in the direction of external magnetic field is three time of the based fluid because of chain-like aggregation [17]. Nevertheless, some research works showed that, the aggregation of nanoparticles can't improve the ETC of nanofluid [18] due to the various aggregation morphology. T. Thaseem [19] reported that, the convective heat transfer coefficient of 5 vol% nanofluid can increase 51% or decrease 32% according to the aggregation morphology.

It is known from Ref. [20] that, there are two kinds of aggregation named reaction limited aggregation, formed when conquering the first potential barrier and diffusion limited aggregation, formed when conquering the second potential barrier. Gaganpreet et al. [21] analyzed the heat transfer of nanofluid from the mesoscopic view and concluded that, loose aggregation including nanolayer (corresponding to diffusion limited aggregation) has lower fractal dimension, larger size and greater ETC. Diffusion limited aggregation grows quickly, and can be broken easily owing to the flow shear [22]. To improve the ETC of nanofluid, Agresti [23] adjusted the aggregation morphology by controlling the PH value of nanofluid. The mechanism could be that, the decrease of the potential barrier due to the very low electrostatic repulsion when PH being adjusted at isoelectric point, leads to greater reaction limited aggregation and lower ETC [24]. Kang [25] presented that, the aggregation morphology effects the ETC and viscosity greatly, more aggregations result in greater ETC and greater viscosity. An interesting phenomenon named shear-reducing effect is reported by Kim [26], the ETC of nanofluid decreases with the increase of shear rate, because the shear of fluid destroys the net-structure of aggregation.

Molecular dynamics simulation is an alternative approach to investigate the heat transfer enhancement by nanofluid, although only mini-system can be simulated because of the great calculation burden. Not a few attempts to explore the mechanism for the increase of ETC of nanoparticle aggregation using molecular dynamics simulations are reported in recent years [27]. There are two kinds of molecular dynamics simulations to obtain the ETC of nanofluid, i.e. equilibrium and non-equilibrium molecular dynamics simulation. Equilibrium molecular dynamics simulation is based on the Green-Kubo equation, and non-equilibrium molecular dynamics simulation instead is based on the definition of ETC [15]. In addition, the potential functions between various molecules are very difficult to ensure. There are practical empirical values of the potential functions for Cu-Ar nanofluid, and Kang et al. [28] described the inter-atomic potential between argon atoms using the well-known Lenard-Jones potential, and describing the interatomic interaction between copper atoms using a more accurate embedded atom method potential. Lee [29] molecular dynamics simulations on the thermal conductivity of nanofluids in aggregated and non-aggregated states were carried out, and indicated that, the thermal conductivity enhancement of aggregated nanofluids is higher compared to non-aggregated nanofluids by up to 35%. Similar works were conducted by Chen [30] and U.A.E. Sharjah [31], and similar conclusions were drawn. Regretly, no quantitative analysis on the influence of fractal dimension on ETC by molecular dynamics is reported so far to our knowledge. The objectives of present work are to quantitatively analyze the influence of fractal dimension on ETC of copper-argon (Cu-Ar) nanofluid, to reveals the underlying mechanisms of heat transfer enhancement by adding nanoparticles with equilibrium molecular dynamics simulations.

## 2. Numerical model

As stated in [11,28], the Cu-Ar nanofluidic system is studied in present work, because it is an ideal choice for an initial molecular dynamics study on thermal conductivity of nanofluid with various aggregation. Indeed, the widely accepted Lenard-Jones potential being two-body potential matches experimental data for bulk fluid argon very well, employs meaningful physical constants as parameters, and has less computation burden than that for multi-body potential. In addition, the calculation precision of heat current in Lammps is higher when two-body potential being applied than that when multi-body potential being applied. Molecular dynamics is a practical numerical simulation method to calculate the state of motion of every atom in the model system based on the Newtons second law.

$$m_i \frac{dv_i}{dt} = F_{ij} = \nabla \varphi_{ij} \tag{1}$$

where $m_i$, $v_i$ is the mass and velocity of $i$th particle (atom or molecule). The resultant force $F_{ij}$ on $i$th particle is the vector sum of all interaction forces between the $i$th particle and $j$th particle ($i \neq j$) within the range of cut-off radius, and can be expressed by the gradient of potential function $\varphi_{ij}$. The positions and velocities of all particles can be calculated by solving Eq. (1). The interested macroscopic physical parameters can be obtained by the means of statistic physics. The description of used molecular dynamic technique involves in four parts, i.e. the choices of potential functions, the calculation of ETC, the calculation of fractal dimension and the setting of parameters.

### 2.1. Choices of potential functions

In this work, Ar is considered as the base fluid. Cu nanoparticle has a face-centered cubic crystal structure with a cubic side of 3.615A [11]. For simplicity, we assume that all Cu atoms in a nanoparticle have the same velocity and acceleration [32]. To obtain the forces between Ar-Ar in MD simulations, the Lenard-Jones potential function $\varphi_{ij}$ read as

$$\varphi_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \quad (r < r_c) \tag{2}$$

where $\varepsilon_{ij}$ is the strength of the potential energy, $\sigma_{ij}$ is scale parameter, $r$ distance between particle $i$ and particle $j$, $r_c$ is the cut-off radius (normally $r_c > 2.5\sigma$, in present work $r_c = 3\sigma$). Note that, $\varphi_{ij} = 0$ when $r \geqslant r_c$.

For the Cu–Cu interatomic interactions, more accurate potential, the embedded atom method potential taking the metallic bonding into account should be employed [33]. However, Lenard- Jones potential was used in present work to reduce the calculation burden, because the objective is to probe into the effect of aggregation morphology on the ETC of nanofluid. The parameters of interaction potential between copper-argon can be obtained by Berthlot combining rule [33], $\varepsilon_{Ar-Cu} = \sqrt{\varepsilon_{Ar-Ar} \cdot \varepsilon_{Cu-Cu}}$, $\sigma_{Ar-Cu} = \frac{\sigma_{Ar-Ar}+\sigma_{Cu-Cu}}{2}$, the details are listed in Table 1. Fig. 1 shows us the potential function

**Table 1**
Parameters of potential functions.

| Atom 1 | Atom 2 | $\varepsilon/10^{-2}$eV | $\sigma$/nm |
|---|---|---|---|
| Ar | Ar | 1.043 7 | 0.340 5 |
| Cu | Cu | 41.015 6 | 0.233 77 |
| Ar | Cu | 6.542 9 | 0.287 1 |