Journal of Molecular Liquids 197 (2014) 14–22

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Investigation of nanoparticle aggregation effect on thermal properties of nanofluid by a combined equilibrium and non-equilibrium molecular dynamics simulation

Mina Sedighi, Ali Mohebbi *

Department of Chemical Engineering, Shahid Bahonar University of Kerman, Kerman, Iran

ARTICLE INFO

Article history:
Received 19 October 2013
Received in revised form 16 March 2014
Accepted 22 April 2014
Available online 5 May 2014

Keywords:
Nanofluid
Aggregation
Thermal conductivity
Specific heat
Thermal diffusivity
Molecular dynamics simulation

ABSTRACT

Many theoretical and experimental studies on heat transfer and flow behavior of nanofluids have been done and the results show that nanofluids significantly increase heat transfer. Nevertheless, there is no accurate understanding from the effect of different mechanisms on nanofluid heat transfer. Computer simulations are a suitable tool for description of physical mechanisms in many processes. In this study, molecular dynamics simulation was used to investigate the effect of nanoparticle aggregation on thermal properties of water-silicon dioxide nanofluid, specifically its thermal conductivity. For calculating nanofluid thermal conductivity a combination of two equilibrium and non-equilibrium molecular dynamics simulations was performed to calculate the specific heat and thermal diffusivity of the nanofluid, respectively. Simulations were performed in NVT ensemble and spherical coordinate. The model was validated by comparison of thermal properties of water base fluid with experimental data in four various temperatures. Results also were compared with theoretical models such as HC model for nanofluid. To investigate the effect of nanoparticle aggregation, two cases of constant and variable volume fractions (i.e. 1.5, 3 and 4.5%) at temperature of 308 K were considered. The results showed that when the aggregation occurs with increasing nanoparticle concentrations, there are an increase in the thermal conductivity and thermal diffusivity of the nanofluid and a decrease in its specific heat. Moreover, when aggregation takes place at constant nanoparticle concentration, the specific heat of nanofluid with suspended nanoparticles did not change with respect to nanofluid with aggregated nanoparticles, but its diffusivity and thermal conductivity increase.

1. Introduction

Cooling systems are one of the most important concerns in factories, industries, transportation and each place that deals with heat transfer. Therefore, in new technologies high heat flow process was created in order to enhance heat transfer. There are different methods for heat transfer improvement [1]. One of them is using the nanofluids instead of current heat transfer fluids. Nanofluids have been prepared by dispersing metallic or non-metallic particles at nanoscale size in ordinary heat transfer fluids. Suspended nanoparticles increase heat transfer by means of increasing the values of nanofluid thermophysical properties. Thermal conductivity of nanofluids is the most important parameter to indicate the heat transfer potential.

Several mathematical models have been presented to predict the nanofluid thermal conductivity [2]. Maxwell's [3] model is the first model in this context. He had predicted that the thermal conductivity of nanofluids is a function of particle volume fraction and thermal conductivity of fluid and solid particles. Later Hamilton and Crosser (HC) [4] by development of Maxwell model and adding a shape factor in it have presented a new model. In addition several models such as Jeffrey [5] and Davis [6] models have been created. All of these models have been investigated in macroscale size and do not consider the solid and liquid movements and consequently probable collisions that cause thermal conductivity enhancement, therefore, they obtained underpredict values in comparison with experimental data.

According to experimental researches [7–9] some parameters can be effective on thermal conductivity coefficient, such as, particle volume fraction, type of nanoparticles, size of particles, and temperature. Hong et al. [9] prepared Fe nanofluid based on ethylene glycol and indicated that thermal conductivity of Fe nanofluid is increased nonlinearly up to 18% as the volume fraction of particles is increased up to 55%. Daungthongsuk and Wongwises [10] experimentally reported the thermal conductivity and dynamic viscosity of TiO_2-water nanofluid. They found that thermal conductivity and viscosity of nanofluids depend on temperature, so that, thermal conductivity of nanofluid increases with increasing temperature and conversely its viscosity decreases. Timofeeva et al. [11] characterized nanofluids of alumina

* Corresponding author. Tel./fax: +98 3412118298.
E-mail addresses: amohebbi2002@yahoo.com, amohebbi@uk.ac.ir (A. Mohebbi).

http://dx.doi.org/10.1016/j.molliq.2014.04.019
0167-7322/

Nomenclatures

C_p	Specific heat at constant pressure
C_v	Specific heat at constant volume
E	Total energy
k	Thermal conductivity
K_B	Boltzmann's constant
r	Radius
t	Time
T	Temperature
U	Potential energy
α	Thermal diffusivity
φ	Particle volume fraction
ρ	Density

Subscripts

Nf	Nanofluid
f	Fluid
p	Particle
th	Theory
MD	Molecular dynamics

particles in water and ethylene glycol using thermal conductivity, viscosity and dynamic light scattering measurements. Their results showed that the thermal conductivity enhancement is within the range predicted by effective medium theory in which the particles are also agglomerated over time. Kathikeyan et al. [12] synthesized CuO nanoparticles with average diameter of 8 nm by a simple precipitation technique and study the thermal properties of the suspensions. The experimental results showed that the nanoparticle size, polydispersity, cluster size, and the volume fraction of the particles have a significant effect on thermal conductivity. The study also mentioned that nanofluids containing ceramic or metallic nanoparticles showed large enhancement in thermal conductivity that cannot be explained by conventional theories.

Except for the parameters that were studied at experimental measurements, investigation of possible mechanisms in molecular scale proves that several other parameters in molecular level are considerable. These factors including Brownian motion of nanoparticles, liquid layering at the liquid/solid interface, nanoparticle clustering and radioactive heat transfer somewhat justify nanofluid's unusual behavior [13]. Nevertheless, generally there is no determinative mechanism in nanofluid studies. Nanoparticle agglomeration is one of the most controversial mechanisms in nanofluid thermal conductivity studies. It has been indicated that when the nanoparticles are suspended in the base fluid, on the effect of Van der Waals forces they are agglomerated over time. This phenomenon has been called nanoparticle aggregation. There are several theories to examine the aggregation effects on the nanofluid's thermal properties and they are described in the following.

Xuan et al. [14] applied the theory of Brownian motion and diffusion-limited aggregation model to simulate random motion and the aggregation process of the nanoparticles. They found that morphology of the suspended nanoparticles besides nanoparticle diameter and volume fraction of nanoparticles is one of the several important factors that affect the thermodynamic properties of nanofluid and that formation of aggregates reduces the efficiency of the energy transport enhancement of the suspended nanoparticles. Prasher et al. [15] used aggregation kinetics of nanoscale colloidal solutions combined with physics of thermal transport to capture the effect of aggregation on the thermal conductivity of nanofluids. Their study developed a unified model, which combines the micro convective effects due to Brownian motions with the change in conduction due to aggregation. The results showed that colloidal chemistry plays a significant role in deciding the conductivity of colloidal suspensions. Jie et al. [16] proposed a new model for thermal conductivity of nanofluids, which is derived from the fact that nanoparticles and clusters coexist in the fluids. The effects of compactness and perfectness of contact between the particles in clusters on the effective thermal conductivity are analyzed. The model showed that the effective thermal conductivity of nanofluids decreases with the increasing concentration of clusters. Feng et al. [17] proposed a new model for effective thermal conductivity of nanofluids based on nanolayer and nanoparticle aggregation. Their study was derived on a model based on the fact that a nanolayer exists between nanoparticles and fluid and some particles in nanofluids may contact each other to form clusters. A governed equation for effective thermal conductivity was developed by both the agglomerated clusters and nanoparticles suspended in the fluids. Wu et al. [18] verified experimentally and theoretically the significance of the effect of the cluster structure, size distribution, and thermal conductivity of solid particles in water. The aggregation kinetics of SiO_2 particles in water base fluid was done by adjusting the pH. Their experiments showed that clustering has no any discernible enhancement in the thermal conductivity even at high volume loading.

Investigation of previous researches showed that there are no conclusive theories for the effect of aggregation on thermal properties of nanofluids. Nanoparticle aggregation creates a condition with lower thermal resistance for heat transfer and causes the thermal conductivity enhancement. On the other hand, this phenomenon can decrease the thermal conductivity of nanofluids, in this case, aggregation of the nanoparticles which may cause instability in the suspension, as well as create low efficiency areas in the liquid.

To evaluate the nanofluid's behavior and investigation of the effect of various factors on it, two Mont Carlo and molecular dynamics simulations [19] have been created. Molecular dynamics simulation was first introduced to study the interactions of hard spheres by Alder and Wainwright [20] in the late 1950s. Later at 1964 Rahman [21] carried out the first simulation using a realistic potential for liquid argon. This method simulates the system by force, velocity and positions of atoms in the system at each time step and its purpose is calculation of macroscopic state of the system with a microscopic model. Molecular dynamics simulation uses the algebraic method to specify the path of atoms, thus, it has particular computational advantages. Presence of the time variable estimates the required time in each simulation. In Monte Carlo simulation to evaluate the time there is no such estimation. There are two equilibrium molecular dynamics and non-equilibrium molecular dynamics approaches for molecular dynamics simulations that have been used by researchers to study the nanofluid's behavior.

Keblinski et al. [13] explored the four possible explanations for increasing thermal conductivity using molecular dynamics simulation: Brownian motion of particles, molecular layering of the fluid at the liquid/solid interface, the nature of heat transport in nanoparticles and the effect of nanoparticle clustering. Eapen et al. [22] performed molecular dynamics simulations of the time-dependent heat current correlation to obtain the systematic, dynamical details at the atomistic level using a model system of Xe base fluid and Pt nanoparticles. Their model indicated that the interatomic interactions between fluid and the nanoparticles can be much stronger than the interaction between fluid particles, as well as nanoparticle interactions, are significant factors to understand the heat transport mechanisms of nanofluids. Galamba et al. [23] calculated the thermal conductivity of molten NaCl and KCl through the Evans–Gillan non-equilibrium molecular dynamics algorithm and Green–Kubo equilibrium molecular dynamics simulations. The EMD simulations performed for a binary ionic mixture and the NEMD simulations assumed a pure system for reasons discussed in their work. They found that the thermal conductivity obtained from NEMD simulations was in very good agreement with that obtained through Green–Kubo EMD simulations for a binary ionic mixture. Galliero and Volz [24] used a non-equilibrium molecular dynamics simulation to