Nonequilibrium molecular dynamics simulation of coupling between nanoparticles and base-fluid in a nanofluid

Hongbo Kang a, Yuwen Zhang b,*, Mo Yang a, Ling Li a

a University of Shanghai for Science and Technology, Shanghai 200093, China
b Department of Mechanical and Aerospace Engineering, University of Missouri, Columbia, MO 65211, USA

A R T I C L E   I N F O

Article history:
Received 28 July 2011
Received in revised form 10 November 2011
Accepted 12 November 2011
Available online 15 November 2011
Communicated by R. Wu

Keywords:
Molecular dynamics
Nanofluids
Coupling factor
Aggregation

A B S T R A C T

The intent of this study is to examine nonequilibrium heat transfer in a copper-argon nanofluid by molecular dynamics simulation. Two different methods, the physical definition method and the curve fitting method, are introduced to calculate the coupling factor between nanoparticles and base fluid. The results show that the coupling factors obtained by these two methods are consistent. The coupling factor is proportional to the volume fraction of the nanoparticle and inversely proportional to nanoparticle diameter. In the temperature range of 90–200 K, the coupling factor is not affected by temperature. The nanoparticle aggregation results in a decrease of the coupling factor.

© 2011 Elsevier B.V. All rights reserved.

Nonanofluids are a new class of nanotechnology-based heat transfer fluids that are devised by stably suspending a small amount (1% vol. or less) of nanoparticles, nanofibers or nanotubes with lengths on the order of 1–50 nm in traditional heat transfer fluids [1]. Researchers have shown that nanofluids exhibit very high thermal conductivity even at low concentrations of suspended nanoparticles [2,3]. Moreover, some researchers have demonstrated that the enhancement of nanofluids’ thermal conductivity increases as temperature increases [4,5], making nanofluids even more attractive as a cooling fluid for devices with high energy density. Bergman [6] pointed out that there exists a large discrepancy in the thermal conductivity enhancement of nanofluids based on the results of different experiments; a simple linear relationship between the thermal conductivity enhancement and the nanoparticle volume fraction is in disagreement with the Hamilton–Crosser [7] model.

Nonequilibrium heat transfer in a layer of nanofluid subject to periodical heat flux was studied by Zhang and Ma [8] who developed a two-temperature model to describe the nonequilibrium heat transfer between the nanoparticle and base fluid:

\[
\varphi (\rho c_p T) \frac{dT_s}{dt} = G(T_f - T_s)
\]

\[
(1 - \varphi) (\rho c_p f) \frac{dT_f}{dt} = keff \nabla^2 T + G(T_s - T_f)
\]

where \( G \) is coupling factor; \( \varphi \) is the volume fraction of the nanoparticle; \( T_s \) is the temperature of nanoparticles; \( T_f \) is the temperature of the base fluid, and \( keff \) is the effective thermal conductivity of the nanofluids.

The two-temperature model represented by Eqs. (1) and (2) is commonly applied to nonequilibrium heat conduction in porous media and passive thermal control systems for electronics [9,10]. Furthermore, if the nanofluid is irradiated by a laser, wherein the biological tissue fills with nanoparticles, the base fluid does not absorb the light energy because it is transparent even though the nanoparticle does. This results in an increase of the nanoparticle temperature. Additionally, nonequilibrium heat transfer can utilize the above two-temperature model to show what occurs between the nanoparticle and base fluid. In the two-temperature model, one of the most important properties is the coupling factor, \( G \), that indicates the intensity of the heat exchange between the nanoparticle and the base fluid. This work addresses nonequilibrium heat transfer in a nanofluid and the coupling factor obtained by molecular dynamics simulation.

The nanofluid studied here is formed by dispersing copper nanoparticles in liquid argon. For brevity, some MD simulation information such as domain size, time step size, and the algorithm used for advancing the system in time are not detailed here as they are reported in the authors’ early work [11].

For a MD simulation, the most important step is to choose an inter-molecular potential that describes the interaction between molecules. In this work, two different potentials are used. One is the well-known Lennard–Jones (L–J) potential that matches the experimental data reasonably well for liquid argon. The other one is

* Corresponding author.
E-mail address: zhangyu@missouri.edu (Y. Zhang).
the embedded atom method (EAM) potential that takes metallic bonding into account and is more accurate in describing the interatomic interaction between metal or alloy atoms.

The interatomic interaction between argon–argon and argon–copper atoms are described by the well-known L–J potential:

\[ \Phi(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] \]

where the L–J potential parameters for copper–argon and argon–argon are \( \epsilon_{Ar-Ar} = 1.67 \times 10^{-21} \text{ J} \), \( \sigma_{Ar-Ar} = 0.3405 \text{ nm} \), \( \epsilon_{Cu-Ar} = 10.4153 \times 10^{-21} \text{ J} \), \( \sigma_{Cu-Ar} = 0.2872 \text{ nm} \) [12]. For the interaction of copper–copper atoms, the EAM potential is used and the total potential energy \( E \) of the atom is given by [13]:

\[ E_i = F_i \left( \sum_{j \neq i} \rho \phi_{ij}(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij}) \]

where \( F_i \) is the embedding energy of atom \( i \) and it is a function of the atomic electron density \( \rho \); \( \phi \) is a short-range pair potential interaction between the atoms \( i \) and \( j \).

According to Zhang and Ma [8], the heat exchange between the nanoparticles and the base fluid can be obtained by:

\[ Q = GV_p(T_s - T_f) \]

where \( V_p \) is the volume of the nanoparticle. Thus, if the amount of the heat exchange, the volume of the nanoparticles and the temperature difference between nanoparticles and the base fluid are known, the coupling factor \( G \) can be obtained from Eq. (5).

A nonequilibrium molecular dynamics (NEMD) simulation [14] is used to calculate the coupling factor. In the simulation, the nanoparticle atom with a minimum velocity is chosen first, followed by the base fluid atom that has the maximum velocity. These two velocities are changed with the system still resting in the energy conservation mode. This procedure was performed every few steps in the simulation causing the temperatures of the nanoparticles and the base fluid to increase and decrease, respectively, which caused a temperature difference between the nanoparticles and the base fluid. As a result, a heat flux from the nanoparticles to the base fluid was generated. When this flux attained the kinetic energy exchange that results from the artificial velocity exchange between the nanoparticle and base fluid atoms, the system reached dynamic equilibrium and the temperatures of the nanoparticles and the base fluid became steady. Therefore, the coupling factor was calculated through Eq. (5). For the 5.5% vol. nanofluid with a 5.384 nm nanoparticle diameter, the resulting coupling factor was \( 4.34 \times 10^{15} \text{ W/m}^3 \text{ K} \). According to Zhang and Ma [8], the coupling factor can be approximately calculated by the following equation:

\[ G = 6 \frac{\text{Nu} \phi_{eff} \cdot d^2}{d^2} \]

where the Nusselt number \( \text{Nu} \) is approximately 2 for the case of pure conduction, and the effective conductivity \( \phi_{eff} \) is 0.171 W/mK [11]. The resulting coupling factor is \( 3.87 \times 10^{15} \text{ W/m}^3 \text{ K} \). Compared with the result obtained by the MD simulation, it is 10.8% lower. This is still valid because 2 is the minimum possible value for the Nusselt number [15]. From the molecular dynamics simulation result, it is suggested that the Nusselt set should be about at the value of 2.2.

The influences of the nanoparticle volume fraction and diameter on the coupling factor were then studied. The coupling factors of the nanofluid that contains a 5.384 nm-diameter nanoparticle with vol. 2.48%, 3.16%, 4.1% and 5.46% are obtained using the molecular dynamics simulation and the results are shown in Fig. 1. The coupling factor linearly increases with increasing nanoparticle volume fraction, which is consistent with Eq. (6). Fig. 2 shows the coupling factor for different nanoparticle diameters but also has the same volume fraction, i.e., 5.46% vol., using molecular dynamics simulation. The coupling factor linearly decreases with increasing nanoparticle diameter. This phenomenon can, once again, be explained by Eq. (6). According to Kang et al. [11], the thermal conductivity of the nanofluids is linearly proportional to the nanoparticle diameter, which reduces the exponent of the nanoparticle diameter to one in Eq. (6). As a result, the coupling factor is linearly, inversely proportionate to nanoparticle diameter.

While the influence of the nanoparticle volume fraction and diameter on the coupling factor of the nanofluid can be studied using the nonequilibrium molecular dynamics (NEMD) method mentioned previously, it is difficult to study how temperature affects the coupling factor of the nanofluid. With this challenge in mind, the authors carried out another NEMD simulation to calculate the coupling factor with temperature parameters. The nanoparticle was first “heated” for a short time (50 time steps, 0.2 ps) using the velocity scaling method until the simulating system came to an equilibrium state spontaneously under the NVE ensemble. Fig. 3 shows the temperature of the nanoparticle obtained by this NEMD method. Since the initial temperature and the specific heat capacity of the nanoparticle and base fluid are all known, the equilibrium temperature was calculated through the conservation of energy. The only unknown is how fast the system will come to the equilibrium state, which is related to the coupling factor of the nanofluid. As can be seen from Fig. 3, the decay of the nanoparticle temperature and the growth of the base fluid temperature are all exponential. A function in the form of \( y = y_0 + Ae^{-t/\tau} \) is used
to fit the simulation result curves as shown in Figs. 4 and 5. The fitting equations are as following:

\[
T_f = T_e - (T_e - T_{f0})e^{-t/\tau} \\
T_s = T_e + (T_{s0} - T_e)e^{-t/\tau}
\]

(7)

(8)

where \( T \) is the temperature; the subscript \( f \) denotes base fluid, \( s \) denotes nanoparticle, \( e \) denotes equilibrium and \( 0 \) denotes initial; and \( \tau \) is time constant which should relate to the coupling factor. If the diffusion term in the two-temperature model, i.e., Eq. (2), is neglected, it can be derived that:

\[
G_\tau = \varphi (\rho c_p) \frac{T_e - T_{f0}}{T_{s0} - T_{f0}}
\]

(9)

which can be used to calculate the coupling factor after the time constant \( \tau \) is obtained through the curve fitting.

The coupling factors of the nanofluids that have a volume fraction of 5.46%, 4.1%, 3.16% and 2.48% with the nanoparticle diameter of 5.384 nm, different nanoparticle temperatures are set. i.e., 110 K, 150 K, 200 K. The resulting equilibrium temperatures are 91.3 K, 100.1 K and 110.0 K, respectively. The coupling factors of the nanofluid in these three cases are \( 4.44 \times 10^{15} \text{ W/m}^3\text{K} \), \( 4.36 \times 10^{15} \text{ W/m}^3\text{K} \) and \( 4.49 \times 10^{15} \text{ W/m}^3\text{K} \), respectively. Thus, nanoparticle temperature has no apparent effect on the coupling factor in this temperature range. Fig. 7 also gives the relationship between the nanoparticle volume fraction and the coupling factor of the nanofluid under different temperatures. This relationship shows that they are still directly proportionate and have the same slope under different temperatures. Compared to the results shown in Fig. 1, it also can be concluded that they are consistent with each other.

Next, the nanoparticle aggregation effect is taken into account. The physical model is described by Kang et al. [16]. The results are obtained using the curve fitting method mentioned above and are summarized in Table 1. If there is no nanoparticle aggregation, the coupling factors are consistent with each other even if there is more than one nanoparticle in the simulation box; if there is nanoparticle aggregation, the coupling factors decrease. In addition, under different nanoparticle aggregation configurations, the coupling factors also differ.

Coupling factors of the nanofluid are calculated using the curve fitting and physical definition methods through nonequilibrium molecular dynamics simulation (NEMD). The coupling factors obtained by these two methods are consistent with each other. The coupling factor is proportionate to the volume fraction of the
Table 1
Summary of the coupling factor obtained by molecular dynamics simulation.

<table>
<thead>
<tr>
<th>Two nanoparticles</th>
<th>Without aggregation</th>
<th>Coupling factor $10^{15}$ W/m$^3$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T = 110$ K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.10</td>
</tr>
<tr>
<td></td>
<td>With aggregation</td>
<td>4.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.42</td>
</tr>
<tr>
<td>Four nanoparticles</td>
<td>Without aggregation</td>
<td>4.29</td>
</tr>
<tr>
<td></td>
<td>Two nanoparticle-pairs</td>
<td>4.32</td>
</tr>
<tr>
<td></td>
<td>Four nanoparticles clustered as a line</td>
<td>3.96</td>
</tr>
<tr>
<td></td>
<td>Four-nanoparticle square</td>
<td>2.74</td>
</tr>
<tr>
<td>Eight nanoparticles</td>
<td>Without aggregation</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>Two triple-nanoparticle clusters and one nanoparticle pair</td>
<td>2.55</td>
</tr>
</tbody>
</table>

**Fig. 7.** Coupling factor with different nanoparticle volume fractions under different temperature conditions.

Support for this work by the US National Science Foundation under grant number CBET-1066917 and the Chinese National Natural Science Foundation under Grant Nos. 50828601 and 51076105 is gratefully acknowledged.

**Acknowledgements**

**References**