Estimation of Thermal Conductivity of Nanofluids Using MD-Stochastic Simulation Based Approach

Sujoy Das, M. M. Ghosh

Abstract—The thermal conductivity of a fluid can be significantly enhanced by dispersing nano-sized particles in it, and the resultant fluid is termed as "nanofluid". A theoretical model for estimating the thermal conductivity of a nanofluid has been proposed here. It is based on the mechanism that evenly dispersed nanoparticles within a nanofluid undergo Brownian motion in course of which the nanoparticles repeatedly collide with the heat source. During each collision a rapid heat transfer occurs owing to the solid-solid contact. Molecular dynamics (MD) simulation of the collision of nanoparticles with the heat source has shown that there is a pulse-like pick up of heat by the nanoparticles within 20-100 ps, the extent of which depends not only on thermal conductivity of the nanoparticles, but also on the elastic and other physical properties of the nanoparticle. After the collision the nanoparticles undergo Brownian motion in the base fluid and release the excess heat to the surrounding base fluid within 2-10 ms. The Brownian motion and associated temperature variation of the nanoparticles have been modeled by stochastic analysis. Repeated occurrence of these events by the suspended nanoparticles significantly contributes to the characteristic thermal conductivity of the nanofluids, which has been estimated by the present model for a ethylene glycol based nanofluid containing Cu-nanoparticles of size ranging from 8 to 20 nm, with Gaussian size distribution. The prediction of the present model has shown a reasonable agreement with the experimental data available in literature.

Keywords—Brownian dynamics, Molecular dynamics, Nanofluid, Thermal conductivity.

I. INTRODUCTION

NANOFLUIDS are promising for advanced heat transfer applications since their thermal conductivities are often much greater than that of conventional heat transfer fluids. Diverse types of nanofluids have been produced and characterized since the last decade by different investigators [1]-[5]. The enhancement in thermal conductivity of nanofluids is found to depend on the type of nanoparticles and base fluid, volume fraction of nanoparticles, temperature of the liquid medium, size and shape of the nanoparticles, type of dispersant used for stabilization, etc.

Theoretical investigation on the thermal conductivity of nanofluids is limited. Although some discrete attempts have been made by some researchers to model the heat transfer of nanofluids [6]-[11], a universally accepted model still does not exist. The mechanism of heat transfer of nanofluids has not been established as yet. Conventional continuum models, such as Maxwell's model [12], Hamilton and Crosser's model [13], etc. underpredict the thermal conductivity enhancement of nanofluids to a great extent. Thus, designing the nanofluids for practical applications is still a real problem.

The present work reports estimation of thermal conductivity of ethylene glycol (EG) based copper nanofluid based on coupled molecular dynamics (MD)-stochastic simulation. The nanoparticles dispersed in the nanofluid are assumed to have a Gaussian size distribution with a mean diameter of 14 nm. It is natural that the nanoparticles would inevitably move in the nanofluid by Brownian motion due to their small size and eventually collide with the heat source at a certain frequency depending on the Brownian motion parameters. MD simulations have shown that during collision of any nanoparticle with the heat source a pulse-like heat transfer occurs. The heat transfer due to this type of collision which is assisted by the Brownian motion leads to the enhancement in thermal conductivity of nanofluids. In the present model the heat transfer during collision of the nanoparticles with the heat source has been estimated by MD simulation, and the Brownian motion of the nanoparticles suspended in the nanofluid and the associated thermal evolution have been tracked with the help of stochastic simulation. By combining MD model with stochastic model the thermal conductivity of the present nanofluid has been estimated as a function of volume fraction loading of nanoparticles.

II. SIMULATION DETAILS

The scheme of simulation for estimating the thermal conductivity of a nanofluid has been outlined here. A block-shaped Fe-heat source (at a temperature of 370 K) which is in contact with an EG based Cu (14 nm mean size)-nanofluid (at a temperature of 298 K) has been considered here. The assumed size distribution of nanoparticles in the nanofluid modeled in the present study is shown in Fig. 1. The particle size considered in the nanofluid ranges from 8 nm to 20 nm, with a Gaussian distribution and a mean size of 14 nm.

S. Das is with the Department of Metallurgical and Materials Engineering, National Institute of Technology Durgapur-713209, West Bengal, India (e-mail: sujoynatural@gmail.com).

M. M. Ghosh is with the Department of Metallurgical and Materials Engineering, National Institute of Technology, Durgapur-713209, West Bengal, India (corresponding author. phone: +91 9434788182; fax: +91 343 2547375; e-mail: mmgnitd@gmail.com).
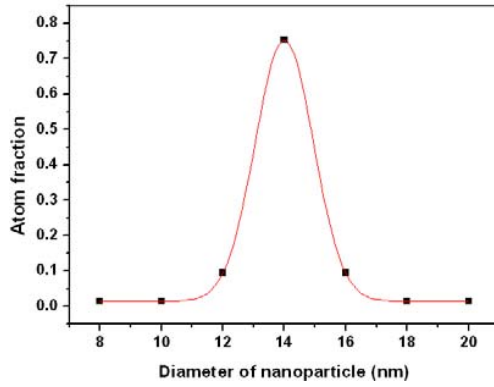
Fig. 1 The assumed size distribution of Cu-nanoparticles present in the EG based nanofluid

It is to be noted here that the transient hot wire method that is used to measure the thermal conductivity of nanofluids uses Pt wire as the heat source. However, interatomic potential for Pt is not available in literature. On the other hand, the interatomic many body (embedded atom method or EAM) potential for Fe is available in literature [14]. The reason behind choosing Fe as the heat source is that the thermal conductivity of bulk Fe is analogous to that of bulk Pt at a temperature of ~370 K and hence the heat extraction characteristics (by conduction mode) during collision of Cu-nanoparticles with Fe-heat source will be same as that with Pt-heat source used in transient hot wire method for measuring thermal conductivity of nanofluids. The nanoparticles within the fluid are expected to move randomly by Brownian motion because of their small sizes. Furthermore, in course of their Brownian motion the nanoparticles will repeatedly collide with the heat source at a frequency, which depends on the Brownian motion parameters like temperature and viscosity of the base fluid, size of the nanoparticle, etc. In order to simulate the heat transfer during the collision the Fe-heat source and Cu-nanoparticles of different sizes are first separately equilibrated at different pre-determined temperatures. Thereafter, the nanoparticles are triggered towards the heat source at a velocity that is pre-calculated on the basis of Brownian motion simulation. During this process the heat source is thermostatted to maintain a constant temperature (370 K), and temperature of both the nanoparticle and heat source have been tracked. In the present study MD simulation for thermal equilibration of both the heat source and nanoparticle has been carried out using NVT ensemble, and the subsequent collision has been modeled using NVE ensemble. 'LAMMPS', the open source MD package has been used for MD simulation of both the thermal equilibration and collision processes. During each collision the nanoparticle will acquire some heat from the heat source. Heat transfer during collision of the nanoparticles with the heat source (evaluated using MD simulation) is found to be very fast due to direct solid-solid contact. The thermal pick up by the nanoparticles during the estimated collision period has been correlated with the initial temperature and size of the nanoparticles. Thus, a series of MD simulations are carried out to generate a database

of heat transfer caused by the collision of nanoparticles of different sizes and initial temperatures, with the heat source. The Brownian motion and thermal modulation during Brownian motion of the nanoparticles suspended in the nanofluid has been evaluated by stochastic simulation based on Brownian dynamics [15]. The coupled multiscale simulation (MD-stochastic) has given rise to estimation of thermal conductivity of the present EG based Cu-nanofluid. In a nanofluid in addition to normal conductive heat transfer through the base fluid itself (without nanoparticles) some amount of heat is carried by the nanoparticles due to their collision with the heat source. The extent of this additional heat transfer has been estimated in order to estimate the enhancement in thermal conductivity of the nanofluid as a function of volume fraction loading of nanoparticles.

The present multiscale model suggests that the collision induced heat transfer depends on the thermal conductivity of the colliding particle as well as the period of collision of the nanoparticle with the heat source. The collision period (Δt_c) is given as [16]:

$$\Delta t_c = \frac{2.94}{V_{coll}} \zeta r_{np} \qquad (1)$$

where

$$\zeta = [\frac{5}{4}\pi^2 \rho V_{coll}^2 (\omega + \omega_{hs})]^{2/5}. \qquad (2)$$

Here V_{coll} is the collision velocity, r_{np} is the radius of the nanoparticle, ρ is the density of the nanoparticle, ω and ω_{hs} are the elasticity parameter for the particle and heat source material, respectively. The elasticity parameter ω for the nanoparticle is defined by [16]:

$$\omega = \frac{1-\mu^2}{\pi E} \qquad (3)$$

where, μ is the Poisson's ratio and E is the Young's modulus. Therefore, apart from size and collision velocity the elastic properties as well as the density of the nanoparticle influence the collision period. In the present theoretical study, the values of μ and E for bulk Pt are taken from literature and used for the calculation of the collision period. Although Fe is taken as the heat source for MD simulation of phononic (conductive) heat transfer process during the collision, but for the calculation of collision period (which depends on the mechanical properties of both the heat source and nanoparticle) the elasticity parameter values (μ and E) available in literature for bulk Pt have been considered, since the elastic properties of Fe are much different from those of Pt. The values of μ and E for the Cu-nanoparticle have been evaluated by some preliminary MD simulation on tensile behavior of nanoparticles [17], and those are used for the calculation of the collision period. Fig. 2 shows the calculated collision period as a function of size of the Cu-nanoparticles dispersed in an EG based nanofluid. It is evident that the

collision period increases markedly with the size of nanoparticles.

The present model has pointed out that thermal as well as elastic and other physical properties of suspended nanoparticles can influence the thermal conductivity of nanofluid. The predictions of the present model have been compared with the experimental data available in literature in order to validate the model.
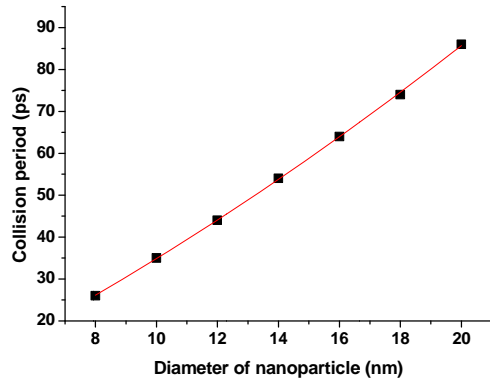

Fig. 2 Calculated collision period of Cu-nanoparticles colliding with a heat source (Pt) in the EG based nanofluid

III. RESULTS AND DISCUSSION

MD simulations have been carried out to simulate the temperature rise of Cu-nanoparticles of diameter ranging from 8 nm to 20 nm, which were initially equilibrated at a predetermined temperature in the range from 298 K to 358 K, during the collision with the Cu-heat source, pre-equilibrated at 370 K. In the MD algorithm EAM potential [14] has been used for both the thermal equilibration and subsequent collision. Fig. 3 (a) shows the estimated time-modulation of temperatures of the Cu-nanoparticles of 14 nm diameter having an initial temperature of 298 K and colliding at a speed of 0.6032 m/s, which is the average speed of the colliding Cu-nanoparticle (14 nm size) as estimated from the preliminary stochastic simulation. It is evidenced from Fig. 3 (a) that the temperature of the Cu-nanoparticle increases almost parabolically with time until it reaches to the heat source temperature. An interesting point to note here is that the nanoparticle is found remained in contact with the heat source during the entire process of heat exchange. It doesn't rebound and hence its temperature continuously rises until the temperature reaches to that of the heat source in a period well beyond the collision period. This is because of the fact that the effect of the surrounding medium has not been considered in the present MD simulation due to non-availability of reliable interatomic potential for Cu-H_2O interactions. Hence, the Brownian force which detaches the nanoparticle from the heat source once the collision period is over is not operative here. The configuration of a Cu-nanoparticle (of 14 nm size) during the process of collision with the heat source has been shown in Fig. 3 (b). It evidences that the nanoparticle remains in contact with the heat source during the process of collision modeled

by the present MD approach. Fig. 3 (a) depicts that the computed temperature of the nanoparticle increases rapidly with time, and for 14 nm size particle, which is pre-equilibrated at 298 K, it (temperature) rises to a value of 310 K within the calculated collision period of 54 ps. Hence, the heat transfer during the collision of the nanoparticle with the heat source is pulse-like or instantaneous. The heat energy received by a Cu-nanoparticle is calculated from its temperature rise during the collision period.
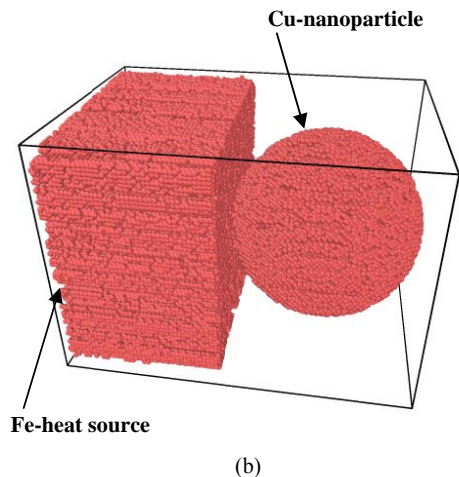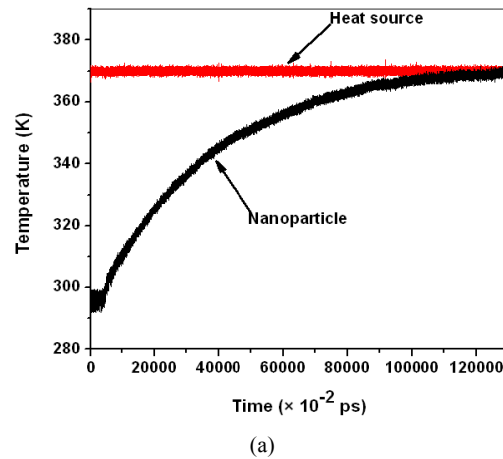

(a)

(b)

Fig. 3 (a) Temperature variation of a Cu-nanoparticle of 14 nm diameter during collision with the Cu-heat source, and (b) configuration of the Cu-nanoparticle during collision with the heat source. The initial temperature of the nanoparticle is 298 K and that of the heat source is 370 K

During the collision a portion of the surface of nanoparticle almost instantaneously picks up the thermal energy from the Cu-heat source due to direct contact, and then this heat-pulse is dissipated throughout the nanoparticle very rapidly owing to the very short distance for the energy transfer. This phenomenon seems to be responsible for the rapid rise in the temperature of the nanoparticle in such a short duration of collision.

MD simulations have been carried out for different initial temperature of Cu-nanoparticles of diameter in the range of 8 nm to 20 nm to estimate the temperature achieved by the nanoparticle at the end of the collision. The database generated by this way have been summarized in Fig. 4, which reveals that for a given size as the pre-collision temperature of the nanoparticle increases the post collision temperature also increases and the variation is almost linear. It is also found that for a given pre-collision temperature as the size decreases the post-collision temperature of the nanoparticles increases.
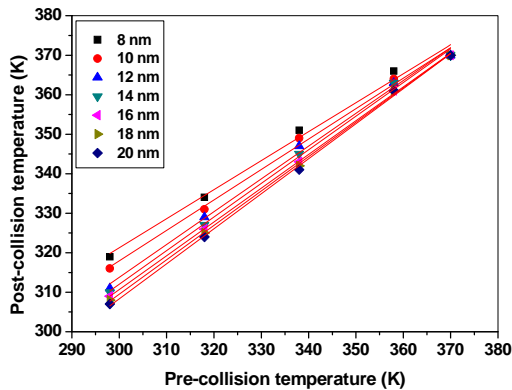

Fig. 4 Post-collision temperature of nanoparticles of different sizes, as a function of their pre-collision temperature
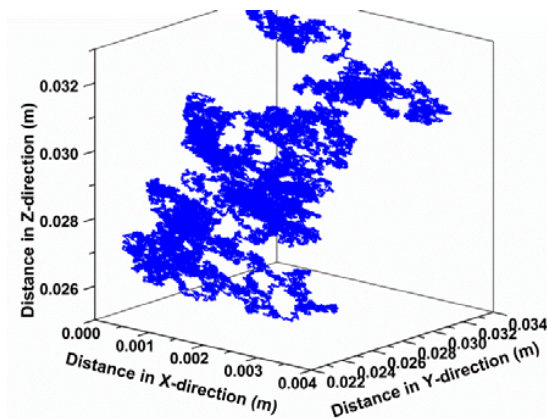

Fig. 5 Trajectory of Brownian motion of a Cu-nanoparticle (14 nm size) in an EG based nanofluid, within the time span of 4.5 s to 6.5 s

The stochastic model considers that the Cu-nanoparticles of diameter in the range of 8 nm to 20 nm suspended in an EG based nanofluid undergo Brownian motion, i.e., move randomly in the base fluid and repeatedly collide with the heat source. Fig. 5 displays the trajectory evaluated by the Brownian dynamics simulation [15] of a Cu-nanoparticle of 14 nm diameter in an EG based nanofluid. It is evident that the nanoparticle moves within the nanofluid in a completely random fashion and eventually collides with the heat source.

After the collision the particle moves in the bulk liquid by Brownian motion, and it exchanges heat with the fluid as per the rule of flow past a spherical particle [8]. The database

generated from MD simulations has been fed into stochastic simulation to obtain the total thermal history of the nanoparticles suspended in the present nanofluid and based on this the thermal conductivity of the nanofluid has been evaluated as a function of volume fraction loading of nanoparticles. The overall thermal modulation of a particle of 14 nm size obtained by the MD simulation coupled with stochastic analysis within a time span of 4.5 s to 6.5 s has been displayed in Fig. 6. The sharp peaks correspond to the pulse-like temperature changes during the collisions with heat source, while the intermediate regions evidence a rapid dissipation of heat by the nanoparticle to the surrounding base fluid. The nanoparticle moving in the base fluid by Brownian motion picks up heat very rapidly (in ~20-100 ps) during collision with the heat source, and subsequently during its motion through the bulk fluid it releases the acquired heat rather fast (in ~2-10 ms) to the base fluid by the conductive and microconvective mechanism. The large specific surface area of the nanoparticles seems to promote the rapid heat transfer during their Brownian motion.

Computations based on MD simulation coupled with stochastic simulation have shown that the energy transfer mechanism proposed in the present model results in an appreciable enhancement in the thermal conductivity of the fluid. The predicted enhancement in the thermal conductivity of the EG based Cu (8-20 nm dia.) nanofluid as a function of the volume fraction of nanoparticles is plotted Fig. 7 on the basis of the proposed energy transfer mechanism alone. It is found that for a given volume percent of loading (≤2.0%), the theoretically estimated enhancement in thermal conductivity is much larger than those predicted by Maxwell's model [12], provided the nanoparticles are assumed to be free from linear or fractal agglomeration. It is to be mentioned here that
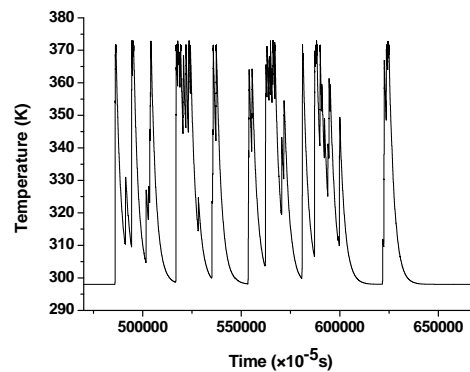

Fig. 6 Simulated thermal history of a Cu particle of 14 nm size moving in EG by Brownian motion within the time period from 4.5 s to 6.5 s

Maxwell's model [12] does not consider Brownian motion assisted collision of nanoparticles suspended in a nanofluid with the heat source and the associated pulse-like heat transfer, which has profound effect in enhancing the thermal conductivity of nanofluids. The Maxwell's model [12] considers the nanoparticles suspended in a nanofluid as static

and hence the enhancement predicted by the Maxwell's model [12] is negligible and far below that predicted by the present model. Based on the proposed energy transfer mechanism, it is predicted that the enhancement in thermal conductivity of an EG based nanofluid would increase linearly with the extent of Cu-nanoparticles loading (≤2.0 vol.%) in the base fluid. These predictions have been compared with the experimental data available in literature [18]. It is evident from Fig. 7 that for a given volume percent of loading (≤2.0 vol.%), the theoretically estimated enhancement in thermal conductivity is well in agreement with the experimentally determined value reported by [18] for EG based Cu-nanofluid. A small deviation between the prediction of the present model and the experimental data [18] may be attributed to the difference in size of the nanoparticles (8-20 nm) considered in the present MD-stochastic model of nanofluid compared to the experimentally prevailing size of the Cu-particles (30-200 nm) in the nanofluid produced by [18]. Considering the smaller size of nanoparticles in the nanofluid modeled in the present study compared to that produced experimentally by [18] a higher value of the enhancement in thermal conductivity of the model nanofluid was expected. Hence, along with the mechanism proposed in the present study operation of some other parallel mechanisms for the heat transfer in nanofluids cannot be ruled out. However, at the same time, the contribution of the present mechanism cannot be ignored and should be taken as a dominant mechanism of heat transfer in a nanofluid. Moreover, the experimental data of EG based Cu-nanofluids show a linear variation in the enhancement in thermal conductivity with the extent of Cu-nanoparticles loading (≤2.0 vol.%) in the base fluid. This nature of variation is in conformity with the predictions of the present model (Fig. 7). Thus, the heat transfer caused by the Brownian motion assisted collision of nanoparticles dispersed in a nanofluid with the heat source, which has been overlooked in the existing models can be thought upon as a dominant mechanism for the enhanced thermal conductivity of nanofluids.
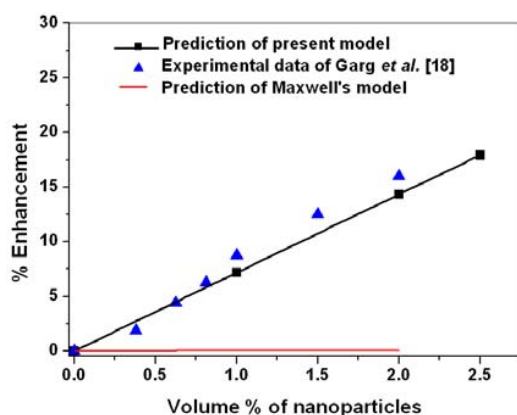

Fig. 7 Enhancement in thermal conductivity with volume fraction of nanoparticles of Cu in EG based nanofluid obtained by [18] compared with the present theoretical prediction for EG based Cu (8-20 nm size)-nanofluid

IV. CONCLUSION

Simulation of thermal conductivity of EG based Cu (8-20 nm size) nanofluid by the present MD-stochastic model has predicted a significant enhancement in the thermal conductivity, which increases linearly with volume fraction loading of nanoparticles. The predicted enhancement in thermal conductivity is well in agreement with the experimental data available in literature.

ACKNOWLEDGMENT

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