Molecular dynamics simulation of thermal conductivity of nanofluids

S L Krasnolutskii and V Ya Rudyak*
Novosibirsk State Architecture and Civil Engineering University (Sibstrin),
113, Leningradskaya St., Novosibirsk, 630008 Russia

*E-mail: valery.rudyak@mail.ru

Abstract. Thermal conductivity of nanofluids has been modeled by means of molecular dynamics method. Nanofluids based on argon with aluminum and zinc particles ranging in size from 1 to 4 nm and particles volume concentration from 1% to 5% have been considered. The dependence of the thermal conductivity coefficient of nanofluids on volume concentration of particles has been studied. It was shown that the thermal conductivity of nanofluid is not described by the classical theories. It depends on the particle size and increases with it. In addition, it has been found that nanofluids with small particles may have even lower thermal conductivity than that of the base fluid. Evolutions of correlation functions that contribute to the thermal conductivity coefficient and integrals from them were studied in details.

1. Introduction

Interest in nanofluids, which arose more than twenty years ago, was motivated largely by the possibility of their various thermophysical applications. Nanofluids can be successfully applied as heat-transfer and cooling agents of different engines and aggregates, especially in electronic systems, for heat power engineering, for transportation of thermal energy, etc. Today it is reliably established that the thermal conductivity of nanofluids is not described by classical theories and usually significantly exceeds the thermal conductivity of conventional coarse-dispersed liquids. In particular, it depends on the particle size and increases with its growth (see, for example, [1, 2]). Concerning of the excess of the thermal conductivity coefficient over the corresponding value for the base fluid, the experimental data are very contradictory. It is usually indicated that it is almost always higher than Maxwell's theory predicts [3]. However, in experiments nanofluids with sufficiently large particles are usually studied. As a rule, their size exceeds 10–15 nm. This is due to the aggregation of ultra-small nanoparticles and the need to use surfactants that significantly change the thermophysical properties of nanofluids and the stronger the smaller the size of nanoparticles. On the contrary, the method of molecular dynamics, having the predictive power of the experiment, allows to realize the purest experiment, particularly to use monodisperse particles. In addition, the measurements of the thermophysical properties of nanofluids give only integral information about their transport processes and as a rule do not answer the question of the mechanisms of these processes. To study the thermal conductivity of nanofluids with small particles and mechanisms of transport processes the molecular dynamics (MD) method is used in this paper.

The MD simulations of the thermal conductivity of nanofluids have been carried by several authors earlier. For example the thermal conductivity of xenon-based nanofluids with platinum nanoclusters
was modeled in [4]. However, that publication had a number of methodical drawbacks; its authors admitted that the thermal conductivity of the nanofluid, which is a binary system, was calculated using the formula for one-component systems. In this study, we consider model nanofluids with argon as the carrier fluid and with spherical aluminum and zinc nanoparticles. The nanoparticle size was varied in the range of 1–4 nm, and their volume concentration was varied in the range of 1–5%.

2. The simulation technique
In simulation, we employed the standard MD method. The original SibMD package was used. Earlier this package was applied for solving various problems in the theory of transport of nanofluids [5–7]. The simulation was carried out in a cubic cell with periodic boundary conditions. The interaction of molecules of the carrier fluid was described by the Lennard-Jones potential. The interactions of molecules of the carrier fluid with a nanoparticle and nanoparticles each other were determined by the RK [8] and RKI [9] potentials respectively. In all calculations the pressure of the nanofluid is equal to the pressure of the carrier fluid with a preset density. Since the phase trajectories of the system are locally unstable and mixed in MD calculation [10, 11], the results obtained must be averaged over the ensemble of independent phase trajectories. In this study, averaging was carried out over 1000 independent phase trajectories.

The parameters of the interaction potential for the argon molecules were as follows: \( \sigma = 3.405 \, \text{Å} \) and \( \frac{\varepsilon}{k_B} = 119.8 \, \text{K} \) [12]. To calculate the parameters of potentials RK and RKI, we used the following parameters of the Lennard-Jones potential: \( \sigma = 2.46 \, \text{Å} \) and \( \frac{\varepsilon}{k_B} = 1040 \, \text{K} \) for zinc [13] and \( \sigma = 2.551 \, \text{Å} \) and \( \frac{\varepsilon}{k_B} = 857.6 \, \text{K} \) for aluminum. The latter parameters were obtained from the data on the Young modulus and the crystal lattice structure. Parameters of intermolecular potentials for different substances were determined by means of simple combination relations \( \sigma_{ij} = \sqrt{\sigma_i \sigma_j} \) and \( \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \). In all presented examples the density of nanofluids is equal to \( \rho = n \sigma^3 = 0.707 \), and temperature \( T = 300 \, \text{K} \).

The thermal conductivity of a nanofluid was calculated by means of so named Green–Kubo formulas. To calculate the thermal conductivity coefficient of nanofluid it is necessary to exclude the heat diffusive flux. Thus, the thermal conductivity coefficient is determined as [14, 15]

\[
\lambda = \lambda_0 - \lambda_\phi = \frac{L_0}{T} - \frac{L_\phi^2}{T^2},
\]

The coefficients that appear in this formula are equal to the integrals of equilibrium correlation functions (terms in the angle brackets)

\[
L_0 = \frac{V}{3} \int_0^\tau (j_\phi(0) \cdot j_\phi(t)) \, dt, \quad L_\phi = \frac{V}{3} \int_0^\tau (j_\phi(0) \cdot j_\phi(t)) \, dt, \quad L_\phi^2 = \frac{V}{3} \int_0^\tau (j_\phi(0) \cdot j_\phi(t)) \, dt,
\]

here \( \tau \) is the time of achieving the plateau value [16]. The diffusion flux of nanoparticle \( j_\phi \) and heat flux \( j_\phi \) that appear in these formulas are defined by the relations

\[
j_\phi(t) = 1 \sum_{\alpha = 1}^{N} \langle v_\alpha \rangle(t), \quad j_\phi(t) = \frac{1}{V} \sum_{\alpha = 2, \alpha \neq 1}^{N} \langle v_\alpha \rangle(t) + \frac{1}{V} \sum_{\alpha = 2, \alpha \neq 1}^{N} \langle v_\alpha \rangle(t) + \frac{1}{V} \sum_{\alpha = 2, \alpha \neq 1}^{N} \langle v_\alpha \rangle(t).
\]

The last expression contains three different terms, \( j_\phi^k \), \( j_\phi^p \), and \( j_\phi^c \), which specify the heat flux associated with the transfer of the kinetic and potential energy, as well as the heat flux that appears as a result of the collisions, respectively.

3. Simulation results
A typical dependence of the relative thermal conductivity coefficient \( \lambda_\alpha = \lambda / \lambda_\phi \) of a nanofluid with zinc particles of size 2 nm on the volume concentration of nanoparticles is shown in figure 1. Here, triangles mark the data of simulation and dashed line 2 corresponds to Maxwell’s formula [3]. The
thermal conductivity of the given nanofluid considerably exceeds the thermal conductivity of the carrier fluid as well as of coarse-dispersed liquids. For example, the thermal conductivity of a 2% nanofluid is almost twice as high as the value given by Maxwell’s formula. The dependence of the thermal conductivity coefficient of a nanofluid considered is successfully described by a quadratic dependence on their volume concentration $\phi$ of the form

$$\lambda_r = \lambda / \lambda_f = 1 + a_1 \phi - a_2 \phi^2.$$  \hspace{1cm} (4)

In figure 1, this expression corresponds to the dotted curve 1 (in this case, $a_1 = 63.1$ and $a_2 = 607.9$). The presence of the second term in formula (4) indicates that, upon an increase in the concentration, the thermal conductivity of the nanofluid achieves a certain limiting value. This behavior was also observed in the experiments [2]. On the other hand, the thermal conductivity for low concentrations of nanoparticles (when the second term in formula (4) can be omitted) increases linearly with the concentration. In this case, the relative excess of thermal conductivity $\Delta = (\lambda_r - 1)$ is about 20 times larger than the value predicted by the Maxwell’s theory.

To determine the dependence of the thermal conductivity on the nanoparticle diameter, we considered two nanofluids based on argon with zinc and aluminum nanoparticles. In both cases, the volume concentration of nanoparticles was 4.2%. The results are shown in figure 2. Here, the squares and curve 1 correspond to the nanofluid with zinc particles, curve 2 was obtained for the nanofluid with aluminum nanoparticles, line 3 is the value calculated by Maxwell's formula, and line 4 describes the data for pure argon. The results obtained for these two nanofluids differ significantly. The thermal conductivity of the nanofluid with zinc particles is always substantially higher than the thermal conductivity of the carrier fluid and than the value determined by Maxwell's formula. Conversely, the thermal conductivity of a nanofluid with particle of size 4 nm exceeds the value determined by Maxwell's formula.

In classical theories of the thermal conductivity of fluids with coarse particles, the material of disperse particles is considered in terms of their thermal conductivity [3]. However, the situation in nanofluids with metal nanoparticles is different. In this case, Maxwell's formula becomes independent of the particle material and assumes the simple form $\lambda_r = (1 + 2\phi)(1 - \phi)$. Therefore, classical theories do not in fact yield the dependence of the thermal conductivity of disperse fluids on the particle material. Nevertheless, the results considered here show that this dependence exists. For example, the thermal conductivity of Ar–Zn nanofluid with zinc nanoparticles of diameter 2 nm and a volume concentration of 4.2% is approximately 2.4 times higher than the corresponding value for the Ar–Al nanofluid. How-

Figure 1. Dependence of the relative thermal conductivity coefficient of Ar–Zn nanofluid on the volume concentration of nanoparticles.

Figure 2. Dependences of the relative thermal conductivity coefficients of Ar–Zn and Ar–Al nanofluids on the nanoparticle diameter $d$ (nm).
ever, the density of zinc is also higher than the density of aluminum. Therefore, we can state that the thermal conductivity of a nanofluid depends on the particle material (increases with its density).

4. Analysis of different contributions to thermal conductivity

Analysis of expressions (1)–(3) shows that the thermal conductivity is determined by a number of various contributions. To find the reason for the substantial excess of the thermal conductivity of a nanofluid over the corresponding value for the carrier fluid, we must analyze all these contributions. For the calculation of each of the contributions it is necessary to take into account the corresponding diffusion one. As a result, we can calculate all six contributions to the thermal conductivity coefficient of a nanofluid: kinetic (superscript K), potential (P), collisional (C), kinetic-potential (KP), kinetic-collisional (KC), and potential-collisional (PC) as follows:

\[ \lambda^K = \lambda^K_0 - \lambda^K_d, \quad \lambda^C = \lambda^C_0 - \lambda^C_d, \quad \lambda^{KP} = \lambda^{KP}_0 - \lambda^{KP}_d, \quad \lambda^{KC} = \lambda^{KC}_0 - \lambda^{KC}_d, \quad \lambda^{PC} = \lambda^{PC}_0 - \lambda^{PC}_d. \]

The results of calculations for argon and argon-based nanofluids with zinc particles of diameters 2 and 4 nm for their volume concentration \( \phi = 4.2\% \) and mass concentration \( C_2 = 0.208 \) are given in table 1. The main contribution to the thermal conductivity of pure argon comes from the coefficients \( \lambda^C(62\%) \), which determine the energy flux associated with collisions between argon atoms, and \( \lambda^{KC}(22\%) \), which is associated with the correlation between the kinetic energy flux and the energy flux due to collisions. This is not surprising, since the density of argon is high. In this case, the kinetic heat transfer (\( \lambda^K \)) associated with the motion of molecules only is small and amounts to only 8%.

What is the difference between the thermal conductivity structure for a nanofluid and pure argon? It can be seen from the table that both positive and negative contributions appear for the studied binary systems. Physically, this means that, along with the conventional heat flux, a flux matched with the temperature gradient (negative thermal conductivity) also appears. As for a pure fluid, the collisional contribution \( \lambda^C \) is important; in nanofluids, it is 1.5 times larger for a nanofluid with a particle diameter of 2 nm and 3.6 times larger for a nanofluid with a particle diameter of 4 nm. However, the largest contribution to the thermal conductivity comes from the term \( \lambda^{KC} \). It amounts to 50% of the total thermal conductivity for a nanofluid with 2-nm particles and to almost 80% for a nanofluid with 4-nm particles. Kinetic contribution \( \lambda^K \) is also significant (34% of the total value \( \lambda \) for a nanofluid with a nanoparticle diameter of 2 nm and 45% for a nanofluid with 4-nm particles). Therefore, the higher values of the thermal conductivity of a nanofluid compared to the pure fluid are mainly due to the considerable increase in the kinetic (\( \lambda^K \)) and kinetic-collisional (\( \lambda^{KC} \)) contributions.

Table 1. Contributions of different terms to thermal conductivity, W/(m K).

|          | Ar        | Ar-Zn, \((d = 2 \text{ nm})\) | Ar-Zn, \((d = 4 \text{ nm})\) |
|----------|-----------|-------------------------------|-------------------------------|
| \( \lambda \) | 0.10680659 | 0.268971388                  | 0.795526344                  |
| \( \lambda^K \) | 0.00853276 | 0.0915064848                 | 0.355916415                 |
| \( \lambda^C \) | 0.06503381 | 0.0941946634                 | 0.235283149                 |
| \( \lambda^P \) | 0.00050646 | -0.00676272531               | -0.0225649413               |
| \( \lambda^{KC} \) | 0.02352531 | 0.13499122                   | 0.621340682                 |
| \( \lambda^{KP} \) | 0.00262643 | -0.02207763387               | -0.15062942                 |
| \( \lambda^{PC} \) | 0.00658181 | -0.0241819169                | -0.243819541                |

5. Conclusions

Presented data of the MD simulation of the thermal conductivity of nanofluids have shown that it is not described by the classical theory. The thermal conductivity of nanofluids depends on the size of nanoparticles and their density. What is the reason of such behavior? There are two key factors, the first is as follows: the nanofluid is the specific binary mixture. The correlation of the collision of car-
carrier fluid molecules with the nanoparticles and their motion (the contribution $\lambda_{KC}$, see the table 1) plays the large role in transport of the system energy. On the other hand, the contributions $\lambda_K$ and $\lambda_C$ in nanofluid are larger also than in pure carrier fluid. Detailed analysis of the correlation functions determining the thermal conductivity coefficient (see formulas (2)) has shown that the relaxation times of all these functions were much larger than the corresponding values for pure fluid [17]. This relaxation time coincides with relaxation time of the autocorrelations velocity function of nanoparticles and increases with the increase in their size and density.

The effect of the thermal conductivity excess is determined not only by the nanoparticle size, but also by the density of the nanoparticle material. In this regard, we note that the mass concentration of nanoparticles in nanofluids increases dramatically with increasing density of the particle material. Thus, the excess of the thermal conductivity of a nanofluid over the value for the base fluid is the higher, the higher the mass fraction of nanoparticles. Therefore, the nanofluids with heavy metal particles must have the thermal conductivity higher than the nanofluids with oxide particles at the same volume concentration of the particles.

Acknowledgments

This study was supported in part by the Russian Foundation for Basic Research (project nos. 17-01-00040 and 17-58-45023).

References

[1] Timofeeva E V, Smith D S, Yu W, France D M, Singh D and Rountbort J L 2010 Nanotechnology 21 215703
[2] Pryazhnikov M I, Minakov A V, Rudyak V Ya and Guzei D V 2017 Int. J. Heat Mass Transfer 104 1275–82
[3] Maxwell J C 1873 A Treatise on Electricity and Magnetism vol 1 (Oxford: Clarendon Press) p 496
[4] Eapen J, Li J and Yip S 2007 Phys. Rev. Lett. 98 028302
[5] Rudyak V Ya, Krasnolutskii S L and Ivanov D A 2011 Microfluid. Nanofluid. 11 501–6
[6] Rudyak V Ya and Krasnolutskii S L 2014 Phys. Lett. A 378 1845–9
[7] Rudyak V Ya and Krasnolutskii S L 2015 Tech. Phys. 60 798–804
[8] Rudyak V Ya and Krasnolutskii S L 2002 Tech. Phys. 47 807–13
[9] Rudyak V Ya, Krasnolutskii S L and Ivanov D A 2012 Dokl. Phys. 57 33–5
[10] Norman G E and Stegailov V V 2012 Math. Models Comput. Simul. 5 305–33
[11] Rudyak V Ya 2005 Hydromechanics (Statistical Aerohydromechanics of Homogeneous and Heterogeneous Media vol 2) (Novosibirsk: NSUACE) p 468
[12] Hirschfelder J O, Curtiss C F and Bird R B 1967 Molecular Theory of Gases and Liquids (New York: Wiley) p 1275
[13] Aref’ev K M 1983 Transport Phenomena in Gas and Plasma (Leningrad: Energoatomizdat) p 127
[14] Zubarev D N 1974 Nonequilibrium Statistical Thermodynamics (New York: Consultants Bureau) p 489
[15] De Groot S R and Mazur P 1984 Non-Equilibrium Thermodynamics (New York: Dover publications) p 515
[16] Rudyak V Ya, Belkin A A, Ivanov D A and Egorov V V 2008 High Temperature 46(1) 30–9
[17] Rudyak V Ya and Krasnolutskii S L 2016 Trudy NGASU 19(1) 20–30