Molecular simulation of viscosity of nanofluids based on water with metal particles

S L Krasnolutskii*, A A Belkin and E V Lezhnev
Novosibirsk State University of Architecture and Civil Engineering (Sibstrin),
113, Leningradskaya St., Novosibirsk, 630008 Russia

*E-mail: sergius-l@mail.ru

Abstract. Shear viscosity coefficient of water-based nanofluids with copper particles is simulated with the molecular dynamics method. The interaction of water molecules with each other was modeled with Lennard-Jones potential. The viscosity coefficient was calculated on the basis of the fluctuation-dissipation theorem by the Green–Kubo formula. The selection of parameters of the potential corresponding to the experimental values of water viscosity and density at a given temperature of 25°C at the atmospheric pressure is performed. Rudyak–Krasnolutskii (RK) and Rudyak–Krasnolutskii–Ivanov (RKI) potentials described interaction between nanoparticles and water molecules and nanoparticles with each other, respectively. Diameters of copper nanoparticles used were 2 and 4 nm. Volume concentration of the nanoparticles varied from 1% to 5%. It is shown that the viscosity of the nanofluids exceeds significantly the viscosity of suspensions with macroscopic particles and increases with a decrease in the size of nanoparticles at a fixed volume concentration. The paper also presents the calculation data of pair distribution functions for pure water and nanofluid. It is shown that the water near the nanoparticle is much more structured than in the free volume. This large ordering in the nanofluids is one of the key factors of their higher viscosity compared to pure water.

1. Introduction
Nanofluids have been studied actively for more than 20 years. At present, it is reliably established that their transport properties (thermal conductivity, viscosity, diffusion and thermal diffusion) are not described by classical theories, the basis of which was made by the works of Maxwell and Einstein. In particular, the viscosity and thermal conductivity of nanofluids depend not only on the volume concentration of nanoparticles, but also on their size and material. Although the properties of nanofluids are reliably established experimentally [1,2], the experiments do not allow one to establish the mechanisms of transport processes, since the data obtained are integral characteristics of the studied objects. However, the molecular dynamics (MD) method can be used for this purpose.

Water, despite the apparent simplicity of its chemical formula, is an extremely complex object. Its transport properties still cannot be modeled convincingly by molecular dynamics. Special rather complicated intermolecular potentials were developed for this purpose in 80s of XX century [3]. These are multiparameter potentials, having usually 6 parameters, which are not easy to determine. For this reason, it is still not possible to model well enough, for example, the viscosity and thermal conductivity of water in a wide range of temperatures and pressures [3–5].

It is widely believed that many problems will be solved with the help of quantum mechanical modeling ab initio (from the first principles) [6]. Unfortunately, the ab initio modeling method...
requires a lot of computational resources, and this is its significant drawback. The costs will increase significantly if we additionally take into account the processes of excitation, ionization of atoms and molecules, simultaneous movement of atomic nuclei and electrons, etc., not to mention the exact solution of the corresponding quantum mechanical problem. In addition, there is a problem of determining some parameters used.

Our goal is the simulation of transport processes in nanofluids on the basis of water. As a first step, of course, it is necessary to simulate convincingly and simply the transport processes in water. Our interaction potentials of a nanoparticle with a molecule of carrier medium [7] and nanoparticles between themselves [8] were constructed on the basis of the Lennard-Jones potential earlier. It is therefore natural to use Lennard-Jones potential for water too. In addition, the use of a fairly simple potential of Lennard-Jones can speed up the calculations significantly.

Changes in the structure and enhancement of the short-range order in the carrier fluid associated with the addition of nanoparticles are one of the key causes of changes in the viscosity of nanofluids. The most informative characteristic describing ordering in molecular systems is a pair distribution function \( g_s(r) \) [9,10]. This function characterizes the numerical concentration of molecules in the region at a given distance \( r \) from the center of the selected object (molecule or particle).

The main methods of determining pair distribution functions in homogeneous environments are experiments on scattering and simulation by the MD method. Already the first papers on the modeling of liquefied inert gases showed that the values of the radial distribution function determined by the MD method are in good agreement with the experimental data (see, for example, [11]). Pair distribution functions in water have been studied by the MD method since the 70s of the last century, but such studies do not stop today. This is primarily due to the emergence of new multiparameter potentials for the interaction of water molecules (see [4,5] and the literature cited there). The MD simulation results are in good agreement with the experiments.

One can distinguish different types of structuring in nanofluids. Under certain conditions, nanoparticles form structures [12]. Atoms inside a nanoparticle are also ordered [13]. However, at relatively low volume concentrations of nanoparticles, the main effect on the shear viscosity coefficient of the nanofluid will be caused by a change in the short-range order of the carrier fluid. Short-range order in nanofluid is determined not only by pair distribution function of molecules of the carrier fluid, but also by pair distribution function of nanoparticles and the molecules. At the same time, there are few studies on determination of the pair distribution functions in nanofluids. In paper [14], the pair distribution functions in nanofluid were studied by the MD method. The nanoparticle was modeled as a molecular cluster. However, this cluster was unstable, and such modeling was not quite correct. In [15], RK potential [7] was used to describe the interaction of a nanoparticle with molecules, radial distribution functions in a nanofluid based on liquid argon were studied. The same RK potential, but with other interaction constants, is used in this paper to determine the pair distribution functions in the water-based nanofluids.

The aim of this work is to simulate the shear viscosity of water and water-based nanofluids with copper particles. The diameters of nanoparticles were 2 and 4 nm. The volume concentration of nanoparticles varied from 1% to 5%.

2. The simulation technique

The standard method of molecular dynamics (MD) was used for modeling (see, for example, [16–18]). The free LAMMPS package and the original SibMD package, used in solving various problems of theory of transport processes in nanofluids previously, were applied [19–21]. The simulation was carried out in a cubic cell with periodic boundary conditions. The interaction of water molecules with each other was determined by Lennard-Jones potential

\[
\Phi_{LL}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^12 - \left( \frac{\sigma}{r} \right)^6 \right],
\]
where $\sigma$ is the effective diameter of a molecule, $\varepsilon$ is the depth of the potential well, $r = |r_i - r_j|$ is the distance between the centers of molecules number $i$ and $j$.

The interaction of a water molecule with a nanoparticle was described by the Rudyak–Krasnolutskii (PK) potential [7] (see also [22,23])

$$\Psi(r) = \Psi_i(r) - \Psi_j(r),$$

$$\Psi_i = C_i \left[ \frac{1}{(r-R)} - \frac{1}{(r+R)} - \frac{1}{(r-R)^{\beta}} \right],$$

where $i = 9, 3, a_0 = 9/8, a_3 = 3/2, C_9 = (4\pi\sigma_1^1\sigma_1^2)^2/45V_p, C_3 = (2\pi\sigma_1^1\sigma_1^2)^3/3V_p, V_p^{(-1)} = \rho_p/m_p$. Here $\rho_p$ is density of the nanoparticle material, $m_p$ is mass of a molecule (atom) of the nanoparticle material, $R$ is radius of the nanoparticle, $\sigma_i, \varepsilon_i$ are parameters of the potential (1) of interaction of a water molecule with the nanoparticle molecule.

Rudyak–Krasnolutskii–Ivanov (RKI) potential is used as the interaction potential of nanoparticles [8].

The shear viscosity coefficient was calculated by Green–Kubo relation [24]. Since molecular-dynamic (MD) calculation of the phase trajectories of the system involves their local instability and mixing [18,25], the data obtained should be averaged over the ensemble of phase trajectories constructed independently. In this paper, averaging was performed over at least 1000 independent phase trajectories.

For copper atoms, the parameters $\sigma = 2.2771$ Å, $\varepsilon/k_B = 2800$ K corresponding to the nearest neighbor distance in the crystal lattice at the atmospheric pressure were used. To calculate the potential (2) parameters $\sigma_{12}, \varepsilon_{12}$, the simplest combinational relations $\sigma_{12} = \sqrt[3]{\sigma_1\sigma_2}, \varepsilon_{12} = \sqrt{\varepsilon_1\varepsilon_2}$ were used.

A cubic cell with a side of about 14.9 nm, the number of nanoparticles from 8 to 40 and the number of molecules from 104 to 109 thousands were used to simulate water-based nanofluids with copper particles with a diameter of 2 nm. For nanofluids with particles with a diameter of 4 nm, a cubic simulation cell with a side of about 13 nm, the number of nanoparticles from 1 to 3 and the number of molecules from 69,900 to 72,700 were used. The cell size and the number of molecules changed slightly with the changes in the number of nanoparticles in order to obtain their given volume concentration at the atmospheric pressure.

3. Simulation results

3.1. Simulation of water viscosity

According to the known experimental data on the viscosity [26] and density [27] of water at $T = 25$ °C and atmospheric pressure, the parameters of Lennard-Jones potential $\sigma = 2.9582$ Å, $\varepsilon/k_B = 545.4$ K were determined. Then we used them for MD simulation of nanofluids.

3.2. The viscosity of nanofluids

As a result of MD simulation, the dependence of the viscosity coefficient of the nanofluids on the volume concentration of copper particles in distilled water at $T = 25$ °C was obtained. For convenience, it is presented in a dimensionless form in figure 1. There $\eta$ is the ratio of the viscosity of nanofluids to the one of pure water. Symbols ⋄ and the dash-dotted line correspond to the data for nanofluids with particles of 2-nm diameter, ▲ and the dotted line corresponds to nanofluids with particle diameter of 4 nm, and the dashed line corresponds to the dependence derived by Batchelor [28]. The dependences obtained are linear for small volume concentrations of nanoparticles. With the
increase in the volume concentration of nanoparticles, a quadratic term begins to play a more important role.

Comparison of the presented data shows that in all cases the viscosity coefficient of nanofluids is significantly higher than one of conventional dispersed liquids. Thus, the effective viscosity coefficient of the nanofluids is not described by the classical theories of Einstein and Batchelor even at low concentrations of particles. As the diameter of the nanoparticles increases, the viscosity of the nanofluids decreases. This is consistent with MD simulations of other nanofluids and experiments [1,2].

![Figure 1](image.png)

**Figure 1.** Dependence of the relative viscosity coefficient of water-based nanofluids on the volume concentration of copper nanoparticles

### 3.3. Pair distribution functions

To study the effect of a single nanoparticle on water structure, a simulation cell similar to the one described above was used. The nanoparticle was in thermal equilibrium with the carrier fluid. Numbers of molecules varied from thirteen to fifteen thousands. They were selected in such a way that when the number of molecules increased, the results did not change. The space around the nanoparticle was divided into concentric spherical layers. In each layer, concentration of molecules was determined. Then it was normalized on average concentration in area of the simulation cell undisturbed by the nanoparticle.

The results of modeling the radial distribution functions of pure water molecules and water molecules with copper nanoparticle in nanofluid at a temperature of 298.15 K (25 °C) are presented in figure 2. Distances are measured in nanometers. Diameter of the nanoparticle is equal to 2 nm. Despite the relative simplicity of the interaction model used, it describes well the structure of pure water. In particular, when using multiparameter polyatomic potentials for water, the value of the first maximum of the radial distribution function of oxygen atoms varies from 2.7 (it roughly corresponds to results of experiments) to 3.4 [5]. The result of our simulation for pure water molecules falls within this range.

The addition of nanoparticle structures the liquid further. The value of the first maximum of the radial distribution function of water molecules with the copper nanoparticle is 7.8 as compared to 3.3 for pure water molecules. The following maxima also increase; the region of short-range order grows accordingly. Its characteristic size, determined by the third maximum of the radial distribution function, is 0.67 nm for pure water. And for the nanofluid, comparable deviations from the average concentration of water molecules are observed in the region having size about twice as large as in pure water. And volume of this region increases by about 20 times as compared to one in pure water.

In addition, our simulation of shear viscosity coefficient of the nanofluids showed that it increases with the depth of RK nanoparticle-molecule potential well (2) and the maxima of the pair distribution
function of a nanoparticle and water molecules. This shows the relationship of the effective viscosity of the nanofluids with structuring.

It is useful to compare the size of the structuring region with the characteristic distance between nanoparticles. If the volume fraction of particles with a diameter of 2 nm is 5%, this distance is approximately 2.5 nm. It is clear that the short-range order regions of molecules for neighboring particles overlap in this case, so the entire liquid will be structured by nanoparticles.

![Radial distribution functions of pure water molecules (solid line) and water molecules with copper nanoparticle of 2 nm diameter (dashed line).](image)

**Figure 2.** Radial distribution functions of pure water molecules (solid line) and water molecules with copper nanoparticle of 2 nm diameter (dashed line).

**Conclusions**

Why is it possible to model the viscosity coefficient using such simple interaction potentials as Lennard-Jones (1), RK (2) and RKI ones? Perhaps, it is because that the transport coefficients are integral characteristics of the medium. At the same time, knowledge about the parameters of interaction potentials is usually derived from macroscopic properties of corresponding media. And from these observations 2 parameters of the Lennard-Jones potential can be recovered much more transparently than when working with multiparameter potentials.

**Acknowledgments**

The authors are grateful to Professor Valery Rudyak for scientific advising.

This study was supported in part by the Russian Foundation for Basic Research (project Nos. 17-01-00040 and 19-01-00399).

**References**

[1] Minakov A V, Rudyak V Ya and Pryazhnikov 2018 Colloids and Surfaces A: Physicochemical and Engineering Aspects 554 279–85

[2] Timofeeva E V, Smith D S, Yu W, France D M, Singh D and Routbort J L 2010 Nanotechnology 21 215703

[3] Jorgensen W L, Chandrasekhar J and Madura J D 1983 The Journal of Chemical Physics 79 926–35

[4] Tazi S, Boţan A, Salanne M, Marry V, Turq P and Rotenberg B 2012 Journal of Physics: Condensed Matter 24 284117

[5] Medina J S, Prosmiti R, Villarreal P, Delgado-Barrio G, Winter G, Gonzalez B, Aleman J V and Collado C 2011 Chemical Physics 388 9–18

[6] Zen A, Luo Y, Mazzola G, Guidoni L and Sorella S 2015 The Journal of Chemical Physics 142 144111
[7] Rudyak V Ya and Krasnolutskii S L 2002 *Tech. Phys.* 47 807–13
[8] Rudyak V Ya, Krasnolutskii S L and Ivanov D A 2012 *Dokl. Phys.* 57 33–5
[9] Berne B J and Harp G D 1970 *Adv. Chemical Physics* 17 63–227
[10] Allen M P and Tildesley D J 1987 *Computer Simulation of Liquids* (New York: Oxford University Press) p 408
[11] Yarnell L, Katz M J, Wenzel R G and Koenig S H 1973 *Phys. Rev.* 7 2130
[12] Ohara P C, Leff D V, Heath J R and Gelbart W M 1995 *Physical Review Letters* 75 3466–70
[13] Baletto F, Mottet C and Ferrando R 2003 *Physical Review Letters* 90 135504
[14] Eapen J, Li J and Yip S 2007 *Phys. Rev. E* 76 062501
[15] Rudyak V Ya and Belkin A A 2019 *Colloid Journal* 81 (to be published)
[16] Rapaport D C The Art of Molecular Dynamics Simulation 1995 (Cambridge University Press) p 549
[17] Norman G E and Stegailov V V 2011 *Nanostrukt. Mat. Fiz. Model.* 4 31–59
[18] Norman G E and Stegailov V V 2012 *Math. Models Comput. Simul.* 5 305–33
[19] Rudyak V Ya, Krasnolutskii S L and Ivanov D A 2011 *Microfluid. Nanofluid.* 11 501–6
[20] Rudyak V Ya and Krasnolutskii S L 2014 *Phys. Lett. A* 378 1845–9
[21] Rudyak V Ya and Krasnolutskii S L 2015 *Tech. Phys.* 60 798–804
[22] Rudyak V Ya and Krasnolutskii S L 1999 *Proc. 21st Int. Symp. on RGD (Toulouse)* vol 1 (Éditions Cépaduès) p 263–70
[23] Rudyak V Ya and Krasnolutskii S L 2001 *Dokl. Phys.* 46 897–9
[24] Zubarev D N 1974 *Nonequilibrium Statistical Thermodynamics* (New York: Consultants Bureau) p 489
[25] Norman G E and Stegailov V V 2001 *J. Exp. Theor. Phys.* 92 879–86
[26] *CRC Handbook of Chemistry and Physics 90 Edition* 2010 ed Lide D R (CRC) p 2760
[27] Tanaka M, Girard G, Davis R, Peuto A and Bignell N 2001 *Metrologia* 38 301–9
[28] Batchelor G K 1977 *J. Fluid Mech* 83 (1) 97–117