Molecular dynamics modeling rheology of nanofluids

© *V.Ya. Rudyak, A.A. Belkin, T.A. Rafalskaya*

Novosibirsk State University of Architecture and Civil Engineering, Novosibirsk, Russia
E-mail: valery.rudyak@mail.ru

The rheology of benzene and nanofluids based on it with spherical particles has been studied by the method of nonequilibrium molecular dynamics. As the shear rate increases, all these fluids become pseudoplastic. Critical values of the shear rates of rheology change and their dependence on the concentration of nanoparticles, their size and material are established. The change in rheology is accompanied by a change in the structure of the studied fluids, which is illustrated by the evolution of the corresponding radial distribution functions.

Keywords: molecular dynamics method, nanofluids, viscosity, rheology.

Studies into the characteristics of nanofluids are motivated by their unusual properties and various possible applications. It was found experimentally that approximately one quarter of all nanofluids with spherical particles are non-Newtonian [1,2]. The rheology of disperse fluids has been studied for a long time [3]. A nonlinear nature of the dependence of the stress tensor on the shear rate is a characteristic feature of rheological fluids; a number of rheological relations have also been established. At the same time, experiments often provide no insight into the cause of a rheology change. Different versions of the molecular dynamics (MD) method, which are called nonequilibrium MD methods [4–6], may be used to retrieve such data. The MD method has been proven efficient in modeling of transfer coefficients of nanofluids [5,7,8]. A fairly small number of papers focused on the rheology of nanofluids have been published (see reviews [9–11]). The so-called Lennard-Jones fluids with a particle size of 1–3 nm and a high concentration of particles (from 7 to 50%) were examined in the majority of these studies. It was established that a non-Newtonian behavior emerges at higher particle concentrations. It was noted in [10] that the rheology is independent of particle size. It was found that the emergence of pseudoplastic behavior depends on the shear rate and the particle concentration. It was stated in [12] that relative viscosity coefficient μ_r is proportional to shear rate $\dot{\gamma}$: $\mu_r \propto \dot{\gamma}^\alpha$, where $\alpha = 0.8$.

These are virtually all the findings made so far. Note that the examined suspensions are hardly equivalent to conventional nanofluids (volume concentrations of particles are too high). It still remains unclear how the rheology of nanofluids changes with an increase in the volume concentration of particles, their size, and the particle material. The aim of this paper is to answer these questions. The rheology of benzene-based nanofluids with copper and aluminum particles 3 and 6 nm in size is examined. Their volume concentration φ was varied from 1 to 6%. The nonequilibrium MD method with modeling of the Couette flow between two plates was used [4,5]. The simulation cell was a rectangular parallelepiped. Periodic boundary conditions were set in directions not bounded by walls. Walls were modeled by a set of copper atoms located at the nodes of a cubic crystal lattice. Constant and differently directed velocities were imparted to them, a linear profile of the mean velocity of molecules was established in the channel, and the needed calculations were then performed. The number of molecules of the base fluid varied from 10 000 to 70 000, while the number of particles varied from 2 to 23.

The Lennard-Jones potential characterized the interaction of fluid molecules with themselves and with wall atoms:

$$\Phi(r) = 4\varepsilon_{\alpha\beta}\left[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6\right],$$

while the potentials from [13] and [14] were used to characterize the interaction of nanoparticles with molecules of the base fluid and with themselves, respectively. The last two potentials have been used efficiently in [7] to study the transfer coefficients of nanofluids. The parameters of the Lennard-Jones potential for benzene, copper, and aluminum were defined as $\varepsilon_{11}/k = 524.3, 1247.0$, and 857.6 K and $\sigma_{11} = 0.517, 0.228$, and 0.256 nm, respectively. Cross parameters were specified by combination relations $\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}$, $\sigma_{12} = \sqrt{\sigma_{11}\sigma_{22}}$. Modeling was performed in LAMMPS [15]. All calculations were carried out at atmospheric pressure and a temperature of 25°C. Viscosity coefficient μ was determined based on shear stress τ of the fluid: $\mu = \tau/\dot{\gamma}$. Since the aim of the present study was to examine the rheology of nanofluids in the bulk, the influence of walls on the results had to be excluded. Preliminary calculations were performed for this purpose in channels with their height varying from 5.9 to 27.5 nm. In the latter case, the influence of walls on rheology was almost nonexistent. Subsequent calculations were performed at this channel height.
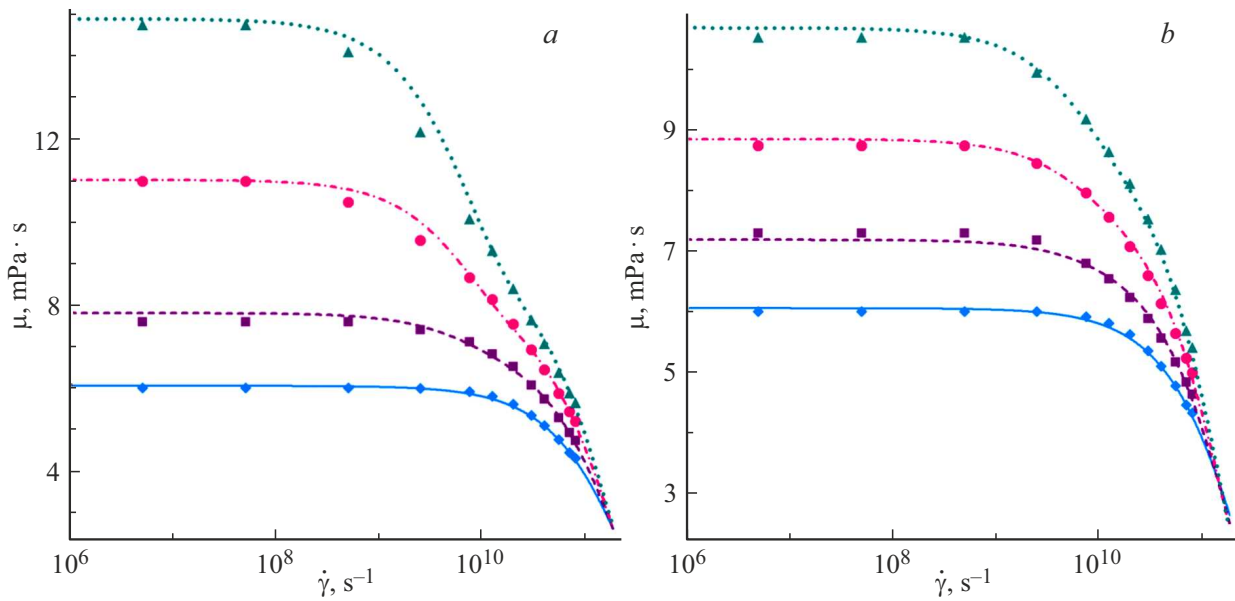
Figure 1. Dependences of the viscosity coefficient on the shear rate of benzene-based nanofluids with copper particles 3 (*a*) and 6 nm (*b*) in diameter.

Critical shear rates at various nanoparticle concentrations φ and two values of nanoparticle diameter d

φ	$\dot{\gamma}_{cr}$, s^{-1}	
	$d = 3$ nm	$d = 6$ nm
0	$1.09 \cdot 10^9$	$1.09 \cdot 10^9$
0.01	−	$1.17 \cdot 10^9$
0.02	$5.33 \cdot 10^8$	$5.03 \cdot 10^8$
0.04	$5.17 \cdot 10^7$	$5.03 \cdot 10^8$
0.06	$5.17 \cdot 10^7$	$5.03 \cdot 10^8$

The first goal was to establish the dependence of rheology of a nanofluid on the particle concentration. Figure 1, *a* illustrates this, presenting the dependences of the viscosity coefficient on the shear rate of a nanofluid with copper particles 3 nm in diameter. Calculated data are represented by symbols and correspond to volume concentrations $\varphi = 0$, 0.02, 0.04, and 0.06 (bottom to top). Curves are the results of approximation of these data. The lower curve corresponds to benzene. At a minimum shear rate, the viscosity coefficient agrees well with the experimental value of 6.04 mPa · s [16]. As the shear rate increases, all fluids (benzene included) become pseudoplastic. The change in rheology is a threshold-type effect. This has already been noted in simulations for an ionic liquid [17]. The lower the particle concentration is, the higher is the shear rate at which the transition from Newtonian rheology to a non-Newtonian behavior occurs. The corresponding data for critical shear rates $\dot{\gamma}_{cr}$ are listed in the table. These values are approximated well by relation $\dot{\gamma}_{cr} = 2 \cdot 10^7 + 1.07 \cdot 10^9 \exp(-60\varphi)$.

The non-Newtonian branch of rheological curves in Fig. 1, *a* is characterized well by the model of a power-law fluid: $\mu = k\dot{\gamma}^{n-1}$. However, index *n* and consistency parameter *k* are functions of both the particle concentration and the shear rate. As the particle concentration increases, the fluid index decreases, while the consistency parameter grows.

In the Newtonian regime, the viscosity coefficient of a nanofluid is given by [2]

$$\mu = \mu_0(1 + a\varphi + b\varphi^2). \qquad (1)$$

The nanofluid in Fig. 1, *a* has $a = 8.38$ and $b = 300$. These values are significantly higher than those predicted by classical theories for fluids with large particles [18]. The nature of dependence (1) remains unchanged as the shear rate increases. For example, the following coefficients are obtained at $\dot{\gamma} = 8 \cdot 10^{10}$ s^{-1}: $a = 4.7$, $b = 10$. The second important issue concerns the dependence of rheology of nanofluids on the particle size. The data for a benzene-based nanofluid with copper particles 6 nm in diameter are presented in Fig. 1, *b*. Comparing the data in Fig. 1, one finds that the viscosity of Newtonian nanofluids depends on the particle size (decreases as particles grow larger). This agrees with the available data (see [2,7]). The viscosity coefficient is characterized by relation (1), where $a = 7.13$ and $b = 107$ in the Newtonian regime, while the non-Newtonian regime has the following parameters corresponding to it: at $\dot{\gamma} = 8 \cdot 10^{10}$ s^{-1} $a = 2.87$, $b = 25$.

The dependence of the viscosity coefficient of a nanofluid on the particle material was first established in MD simulations and then verified experimentally [2]. The dependences of viscosity on the shear rate for benzene-based nanofluids with copper and aluminum particles 3 nm in diameter are
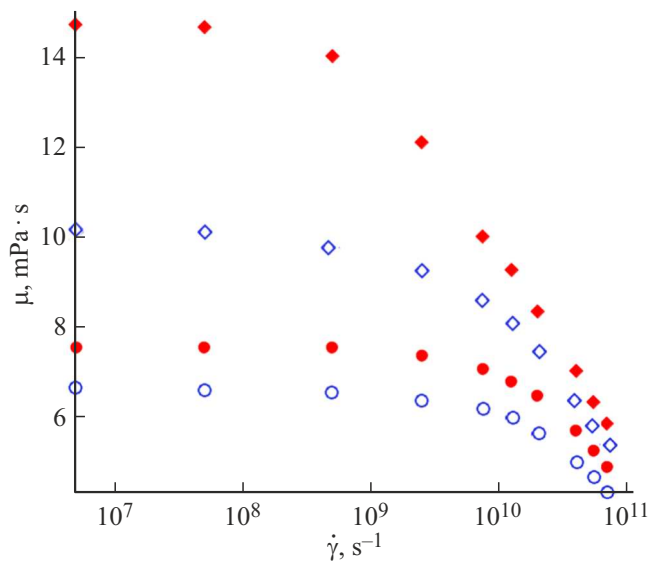
Figure 2. Comparison of viscosity coefficients of nanofluids with copper and aluminum particles.

compared in Fig. 2. Filled and open symbols correspond to copper and aluminum particles, respectively. The data for two concentrations are presented: $\varphi = 0.02$ and 0.06 (bottom to top). The viscosity and rheology of nanofluids do indeed depend on the nanoparticle material, and the viscosity of a nanofluid with copper particles is noticeably higher than the one of a nanofluid with aluminum particles. The change in rheology also occurs at a higher shear rate in the latter fluid. This is related physically to the fact that copper and aluminum particles have significantly different interatomic interaction parameters. Force parameter ε of the Lennard-Jones potential, which governs the structuring of molecules of the base fluid in the vicinity of nanoparticles [7], for copper is almost 1.5 times higher than the corresponding parameter for aluminum.

Structuring of the base fluid [7] is the key factor behind an increase in the viscosity of nanofluids relative to fluids containing large particles. A change in rheology of a nanofluid is associated with a transformation of its structure. The radial distribution function of particles is a fine marker of the fluid structure. Figure 3,a presents radial distribution functions g_2 of benzene-based nanofluids with copper particles 3 nm in diameter ($\varphi = 0.06$). Dashed and solid curves correspond to Newtonian and non-Newtonian (at $\dot{\gamma} = 1.7 \cdot 10^{11}\,\text{s}^{-1}$) nanofluids; the inset shows g_2 of benzene molecules in the bulk. Compared to benzene in the bulk, the nanofluid has several-fold greater first and second maxima. This is indicative of strong structuring of the carrier fluid by nanoparticles. As the shear rate increases, this structuring gets weaker, inducing a reduction in the nanofluid viscosity.

A nanofluid contains molecules of the base fluid and nanoparticles. As particles grow smaller and their concentration increases, they start to form their own short-range order. Figure 3,b shows the values of the nanoparticle–nanoparticle radial distribution function in benzene (system parameters are the same as those indicated above). Dashed, solid, and dash-and-dot curves correspond to a shear rate of $10^6\,\text{s}^{-1}$, $4 \cdot 10^{10}\,\text{s}^{-1}$, and $8 \cdot 10^{10}\,\text{s}^{-1}$, respectively. In the Newtonian regime, the first maximum is approximately 15 times greater than the mean value. A minor maximum around $r = 6$ nm stands out. This is a marker of the emerging short-range order in a nanoparticle ensemble. Short-range ordering of both nanoparticles and molecules is suppressed considerably at higher shear rates.

The data presented in Figs. 1 and 2 (see approximating curves) indicate that the difference in viscosity between nanofluids with various concentrations and the base fluid decreases monotonically with increasing shear rate. Specifically, the viscosity of the nanofluid at the maximum particle concentration in the Newtonian regime was two times higher than the viscosity of benzene, but the ratio dropped to 1.3 at $\dot{\gamma} = 7 \cdot 10^{10}\,\text{s}^{-1}$. This is related to a change in
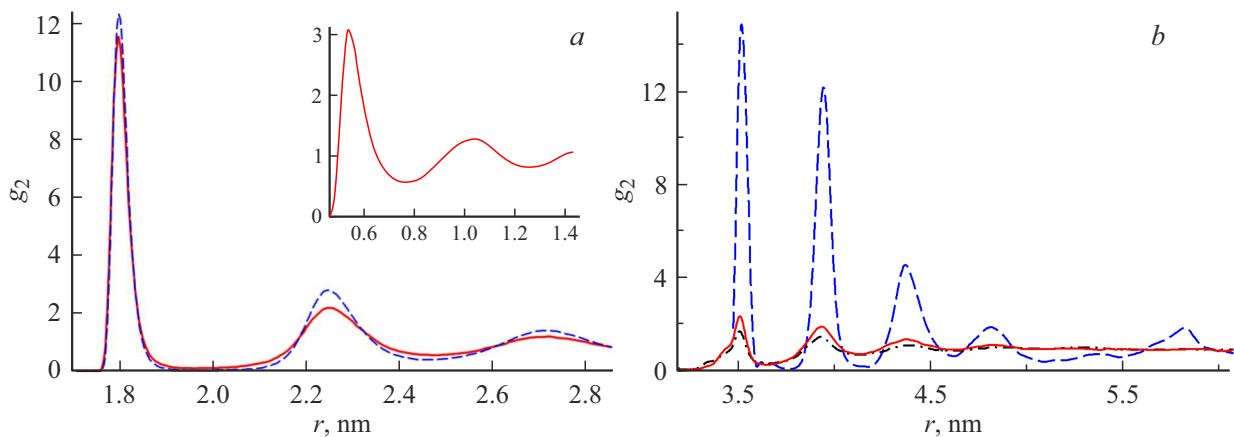

Figure 3. Radial distribution functions of benzene molecules around nanoparticles (a) and nanoparticles in benzene (b) at different shear rates.

the mechanism of momentum equalization in the system at higher shear rates.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.K. Sharma, A.K. Tiwari, A.R. Dixit, Renew. Sustain. Energy Rev., **53**, 779 (2016). DOI: 10.1016/j.rser.2015.09.033

[2] V.Ya. Rudyak, Interfac. Phenom. Heat Transfer, **9** (2), 29 (2021).
DOI: 10.1615/InterfacPhenomHeatTransfer.2021035919

[3] R.P. Chhabra, J.F. Richardson, *Non-Newtonian flow and applied rheology* (Butterworth–Heinemann, Oxford, 2008).

[4] D.C. Rapaport, *The art of molecular dynamics simulation* (Cambridge University Press, Cambridge, 2004).

[5] F. Jabbari, A. Rajabpour, S. Saedodin, Chem. Eng. Sci., **174**, 67 (2017). DOI: 10.1016/J.CES.2017.08.034

[6] N.D. Kondratyuk, V.V. Pisarev, Phys. Usp., **66** (4), 410 (2023). DOI: 10.3367/UFNe.2021.11.039102

[7] V.Ya. Rudyak, A.A. Belkin, S.L. Krasnolutskii, in *Advances in molecular dynamics simulations research*, ed. by S. Köhlerd (Nova Science Publ., N.Y., 2021), p. 1–86.

[8] I. Topal, J. Servantie, Chem. Phys., **516**, 147 (2019). DOI: 10.1016/j.chemphys.2018.09.001

[9] D.S. Devarajan, P. Nourian, G.B. McKenna, R. Khare, J. Rheology, **64**, 529 (2020). DOI: 10.1122/1.5125142

[10] P.J. in't Veld, M.K. Petersen, G.S. Grest, Phys. Rev. E, **79** (2), 021401 (2009). DOI: 10.1103/physreve.79.021401

[11] H. Li, H. Tian, Y. Chen, S. Xiao, X. Zhao, Y. Gao, L. Zhang, J. Phys. Chem. B, **127** (15), 3596 (2023).
DOI: 10.1021/acs.jpcb.3c01697

[12] W.P. Krekelberg, T.M. Truskett, V. Ganesan, Chem. Eng. Commun., **197** (1), 63 (2009).
DOI: 10.1080/00986440903070718

[13] V.Ya. Rudyak, S.L. Krasnolutskii, Tech. Phys., **47** (7), 807 (2002). DOI: 10.1134/1.1495039

[14] V.Ya. Rudyak, S.L. Krasnolutskii, D.A. Ivanov, Dokl. Phys., **57** (1), 33 (2012). DOI: 10.1134/S1028335812010053

[15] A.P. Thompson, H.M. Aktulga, R. Berger, D.S. Bolintineanu, W.M. Brown, P.S. Crozier, P.J. in't Veld, A. Kohlmeyer, S.G. Moore, T.D. Nguyen, R. Shan, M.J. Stevens, J. Tranchida, C. Trott, S.J. Plimpton, Comput. Phys. Commun., **271**, 108171 (2022). DOI: 10.1016/j.cpc.2021.108171

[16] A.I. Volkov, I.M. Zharskii, *Bol'shoi khimicheskii spravochnik* (Sovremennaya Shkola, Minsk, 2005) (in Russian).

[17] O. Borodin, G.D. Smith, H. Kim, J. Phys. Chem. B, **113** (14), 4771 (2009). DOI: 10.1021/jp810016e

[18] G.K. Batchelor, J. Fluid Mech., **83** (1), 97 (1977). DOI: 10.1017/S0022112077001062

Translated by D.Safin