

Molecular modeling viscosity of hybrid nanofluids with carbon nanotubes and copper nanoparticles

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ABSTRACT Molecular dynamics method was used to study the viscosity coefficients of benzene-based hybrid nanofluids with single wall carbon nanotubes and copper nanoparticles. The dependence of the viscosity of these nanofluids on the concentration of carbon nanotubes and nanoparticles, as well as on their morphology was studied. It was shown that viscosity of all the studied nanofluids is significantly higher than that of the base fluid and conventional coarse-dispersed fluids. The viscosity coefficient of nanofluid with carbon nanotubes at a given concentration increases with increasing their length (aspect ratio). At equal concentrations, the viscosity of hybrid nanofluids significantly exceeds the viscosity of nanofluid with nanoparticles or carbon nanotubes and increases with decreasing in nanoparticle size. One of the principal factors responsible for the observed increase in the viscosity of nanofluid is the structuring of the base fluid molecules near the nanoparticles or carbon nanotubes.

KEYWORDS carbon nanotube, hybrid nanofluids, molecular dynamics method, nanofluids, nanoparticles, structure of nanofluid, viscosity

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1. Introduction

Nanofluids (NF), whose active study commenced approximately thirty years ago, have been called dispersed fluids with solid nanoparticles (ranging in size from 1 to 100 nm). Later, after the creation of various production technologies of carbon nanotubes (CNTs), dispersed fluids with CNTs were also called NFs. Initially, interest in nanofluids was driven mainly by their potential use in various applications. Today, NFs are used or are planned to be used in biomedical and cosmetology technologies, in various thermophysical applications, in tribology, in the creation of new materials and coatings, etc. [1–7]. Later it became clear that NFs are an unusual dispersed fluid. Their thermophysical properties are not described by classical theories [7]. One of the main properties of NFs is their viscosity. By now, the viscosity of NFs with conventional spherical nanoparticles (NPs) has been well studied. It has been found that the dependence of the NF viscosity on NP concentration is described by a parabolic function [7–10], however, in addition, it also depends on the size of NPs [7, 10–12] and their material [7, 10, 13]. It is important to emphasize that the viscosity of these NFs is greater the smaller the size of the NPs.

By now, the properties of NFs with CNTs have also been experimentally studied quite well (see [7, 14–18] and the references therein). First of all, it was found that the viscosity and rheology of NFs are determined by the type of CNTs, which can be either single-walled (SWCNTs) or multi-walled (MWCNTs). The viscosity of NFs with SWCNTs is significantly higher than that of NFs with MWCNTs at the same weight concentrations. In addition, it was established that even at sufficiently low concentrations of SWCNTs the corresponding NFs become non-Newtonian and exhibit appeared percolation structure. The presence of percolation also results in the viscoelastic properties appearing in the NFs.

The significant difference in the morphology of NPs and CNTs and the corresponding nanofluids has initiated the creation of another new type of dispersed fluids, called hybrid nanofluids (HNFs). Two distinct classes of HNFs can be identified. The first class comprises NFs wherein two (and sometimes, three) grades of conventional NPs are used. The second class of HNFs is prepared using CNTs and conventional NPs. The great interest in hybrid nanofluids is primarily due to their high thermal conductivity compared to conventional nanofluids. The thermophysical properties of HNFs have been actively studied for approximately a decade. In the preceding five to seven years, approximately two dozen specialized reviews have been appeared, with some of these available in [19–27]. This is due to two factors: the amazing properties of HNFs and their almost infinite diversity (the number of combinations of base fluids, types of NPs and CNTs is very large). Such a great diversity has led to a huge number of experimental facts in the literature indicating the unusual properties of HNFs. Unfortunately, the lack of systematicity in these data does not yet allow answering the

question of what accounts for these unusual properties and whether they can be predicted. For this reason, in order to understand the qualitative impact of concentration, size, and material of CNTs and NPs on the thermal conductivity and viscosity of HNFs, it is essential to employ molecular dynamics (MD) method. This will also facilitate the elucidation of the mechanisms governing transport processes in such NFs.

To date, simulation of HNFs with CNTs and NPs has not been performed employing MD method. In the only paper [28] that we are aware of, the viscosity and thermal conductivity of water-based HNFs with copper and silver particles were studied by the MD method. The volume concentration of NPs in this study ranged from 3 to 9 %; however, this was achieved by increasing the size of the NPs, which varied from 1.21 to 1.75 nm. It was found that the viscosity of HNFs in all cases was higher than that of NF with separately added copper or silver particles. At the same time the viscosity of Ag-containing NF was higher than that of Cu-containing. However, it should be understood that changing the size of nanoparticles we get different nanofluids in all cases. These nanofluids cannot be compared at all.

The objective of the present work is to conduct MD simulations and a systematic study of the viscosity of benzene-based HNFs with SWCNTs and copper NPs. The selection of benzene as the base fluid was predicated on the fact that SWCNTs are hydrophobic, rendering the formation of a water-based nanofluid containing them unfeasible without the use of surfactants. Conversely, SWCNTs exhibit lyophilic behavior towards benzene, as well as a range of other alcohols (isopropanol, ethylene glycol, etc.). Armchair SWCNTs with chirality (8,8) were used as nanotubes with a diameter of 1.1 nm and lengths of 1.1, 3.5, 7.2, and 14.6 nm. The SWCNTs comprised 160, 480, 960, and 1920 carbon atoms, respectively. The diameter of copper nanoparticles was 1.39, 2.5, and 3.2 nm, respectively. In the simulation, the number of SWCNTs ranged from 4 to 48, while the number of nanoparticles ranged from 6 to 24. The number of benzene molecules in the simulation cell ranged from 6,700 to 38,000. The weight concentrations of nanotubes were 3, 9, and 15 %, which was approximately equivalent to a volume concentration of 1, 3, and 5 %. The complexity of objective interpretation of the obtained results required the parallel simulation of the viscosity of NFs containing separately CNTs and copper NPs. The comparison of the MD viscosity data of the NFs with CNTs and Cu NPs was partially done in paper [29]. These data and some new ones will be used in the present paper.

In all cases, the following questions were required to be addressed: (i) What is the effect of the aspect ratio (nanotube length-to-diameter ratio) of CNTs on the viscosity of HNFs? (ii) How does the viscosity of HNFs depend on the concentration of CNTs and NPs? (iii) How does the viscosity of HNFs depend on the length of CNTs? (iv) What is the correlation between the viscosities of HNF and NFs with CNTs and spherical NPs?

2. Simulation technique

The viscosity of a fluid is determined by the momentum dissipation occurring within the system. The shear viscosity coefficient is determined by the fluctuation-dissipation theorem, which is also known as the Green–Kubo formula [30–32]:

$$\eta = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}(0) : \mathbf{J}(t) \rangle dt = \frac{V}{k_B T} \int_0^{\tau_p} \chi_\eta(t) dt, \quad (1)$$

where the microscopic momentum flux tensor of the considered mixture has the form

$$\mathbf{J} = \frac{1}{V} \left(\sum_{\alpha=1}^3 \sum_{i=1}^{N_\alpha} m_\alpha \mathbf{v}_i \mathbf{v}_i + \frac{1}{2} \sum_{\alpha,\beta=1}^3 \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \mathbf{F}_{ij} \mathbf{r}_{ij} \right). \quad (2)$$

Here indices $\alpha, \beta = 1$ refer to the molecules of the carrier fluid, index 2 refers to the nanotube atoms, while index 3 refers to the nanoparticles, m_i is the mass of the corresponding particle (molecule of the carrier fluid, nanotube atom, or nanoparticle), V is the volume of the system, T is the temperature of the medium. $\mathbf{F}_{ij}$ is the force acting on the particle (molecule or nanoparticle), $\mathbf{v}_i$ is the velocity of molecule i , $\mathbf{r}_{ij}$ is the radius-vector between the centers of interacting particles, k_B is the Boltzmann constant, N_α and N_β are the numbers of the carrier fluid molecules, nanotube atoms, or nanoparticles, respectively. The angle brackets in (1) denote ensemble averaging.

According to (1), the viscosity coefficient is a function of time. Its actual (measurable) value is achieved only when the function $\eta(t)$ reaches a plateau value, the duration of which is determined by the time τ_p [32]. During this period, the autocorrelation function of the viscosity $\chi_\eta(t)$ decays. The calculation of this correlation function requires the determination of the microscopic momentum flux tensor $\mathbf{J}(t)$ at successive time moments. This requires knowing the positions $\mathbf{r}_i(t)$ and velocities $\mathbf{v}_i(t)$ of all particles in the system. In the MD method, these phase variables are determined as a result of solving the corresponding Newton equations.

The dynamics of the phase variables of the systems under consideration are determined by the interaction of the constituent particles. Each CNT was simulated as a set of carbon atoms interacting with one another via the AIREBO potential [33]. The interaction between benzene molecules and carbon or copper atoms was determined by the Lennard–Jones potential

$$\Phi_{LJ}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right], \quad (3)$$

where σ_{ij} is the effective diameter of molecules (atoms), ε_{ij} is the depth of the potential well, $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the centers of molecules i and j .

The following potential parameters (3) were used for benzene molecules: $\sigma_1 = 5.034 \text{ \AA}$, $\frac{\varepsilon_1}{k_B} = 544.3 \text{ K}$ [29]. The potential parameters for carbon atoms belonging to different CNTs were sourced from [34]: $\sigma_2 = 3.4157 \text{ \AA}$, $\frac{\varepsilon_2}{k_B} = 27.7 \text{ K}$. Finally, the parameters of the interaction potential of copper atoms were selected based on the viscosity of fluid copper at a temperature of 1356 K and pressure of 1 atm [35] and were equal to: $\sigma_3 = 2.2268 \text{ \AA}$, $\frac{\varepsilon_3}{k_B} = 2255.3 \text{ K}$.

The parameters of the interaction potential (3) of the carrier fluid molecule with a carbon atom of CNT or a nanoparticle atom were calculated using combinatorial relations [36]: $\sigma_{12} = \sqrt{\sigma_1 \sigma_2}$, $\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$. Since the potential (3) has an infinite radius of action, it was truncated in the course of simulation process, the truncation radius was equal to $2.5 \sigma_i$ ($i = 1, 2$).

One of the most challenging aspects of simulating NFs with NPs and NPs with each other is the construction of the corresponding interaction potentials. These potentials are known as the Rudyak–Krasnolutsii (RK) [37] potential and the Rudyak–Krasnolutsii–Ivanov one (RKI) [38]. They were derived on the assumption that the NPs are solid and spherical. These potentials are discussed in details in [29, 32].

The NF was simulated using the conventional MD method [39], with the LAMMPS software [40] employed for this purpose. The simulation was conducted in cubic cells with periodic boundary conditions. At the initial moment, benzene molecules were uniformly distributed within the cubic simulation cell, with the exception of the volume occupied by CNTs and NPs. The initial velocities of the carrier fluid molecules, CNT and NP atoms were set in accordance with the Maxwell distribution at a given temperature. The calculation commenced following an initial relaxation period of 1 – 2 ns, during which the simulated system attained equilibrium at a given temperature and pressure. Typical screenshot for HNF with NPs diameter 1.6 nm and CNT with length 14.6 nm are presented in Fig. 1. Here the volume concentrations of the NPs and CNTs are equal to 2 and 1 %, correspondingly.

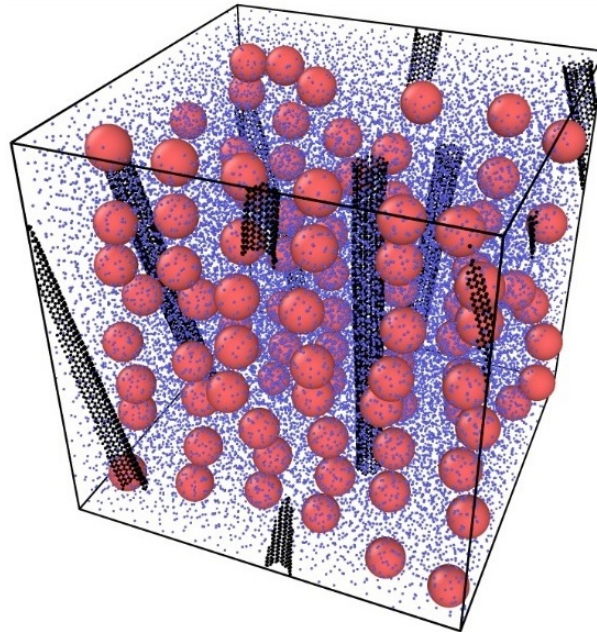


FIG. 1. Screenshot of a hybrid nanofluid simulation cell

The Verlet scheme was employed for the integration of Newton's equations. The NPT Nosé–Hoover thermostat [41, 42] was used, maintaining the given average values of pressure $p = 1 \text{ atm}$ and temperature $T = 25 \text{ }^\circ\text{C}$. It is important to note that the simulation of the nanofluid evolution imposes more stringent constraints on the simulation cell size in comparison to a homogeneous medium. Since the nanotube should not interact with itself, it is necessary that the side length of the cubic cell should be significantly larger than the length of the nanotube. The mean cell size for CNTs with lengths of 1.1 and 3.5 was a minimum of 10.1 nm, while for CNTs with lengths of 7.2 and 14.6 nm it was at least 11.2 and 17.5 nm, respectively. As a consequence of the local instability and mixing observed during the computation of the phase trajectories of the system [43, 44] the obtained data should be averaged over the ensemble of independently constructed phase trajectories. In the present study, the data were averaged over a minimum of 1,000 phase trajectories. The computation time per phase trajectory was 50 ns.

3. Viscosity of nanofluid with carbon nanotubes

In this paper, the viscosity of benzene-based HNFs with CNTs and copper NPs was studied. The analysis of the obtained data requires their comparison with the viscosity of NFs separately with CNTs and copper NPs. Such data were partially obtained earlier in paper [29]. These data are used in the present paper; in addition, some new data necessary for further analysis are presented.

The accuracy of MD modeling was determined in our paper [29]. For this purpose, the viscosity coefficient of pure benzene was simulated at atmospheric pressure and a temperature of 25 °C. It was found that the obtained value (0.6 mPa·s) agrees with high accuracy with the experimental value (0.604 mPa·s [45]). Further, in [29], the dependence of the viscosity of nanofluids with spherical nanoparticles on their concentration and diameter was systematically studied. It has been shown that this viscosity significantly exceeds the corresponding values for coarse-dispersed fluids and increases with decreasing particle size. This is consistent with the existing experimental data [7, 10–12]. The second conclusion obtained in this paper is related to nanofluids with CNTs. The dependence of the viscosity coefficient on the CNT concentration was also studied, showing that it increases with increasing CNT length. However, the nature of this dependence was not explored. The analysis of the last obtained data allows drawing several conclusions. The first conclusion is that the viscosity coefficient of all NFs increases monotonically with rising CNT concentration. This growth is significantly greater than that observed in coarse-dispersed fluids, for which the viscosity is described by Batchelor's theory [46]. Secondly, as the length of the CNTs increases, the viscosity of the corresponding NFs increases rapidly and exceeds the viscosity of NF with copper particles at all concentrations. Figure 2 shows the correlation between the relative viscosity coefficient $\eta_r = \eta / \eta_b$ (η_b is the viscosity coefficient of the based fluid) of NF and the length of CNTs at varying CNT concentrations. The observed increase in the viscosity of the NF with increasing CNT length is well described by the following logarithmic function

$$\eta_r(L) = a(\varphi) \ln(L) + b(\varphi). \quad (4)$$

The parameters $a(\varphi)$ and $b(\varphi)$ in equation (4) are given in Table 1, here φ is the volume concentration of CNTs. These correlations are illustrated in Fig. 2 by means of various lines.

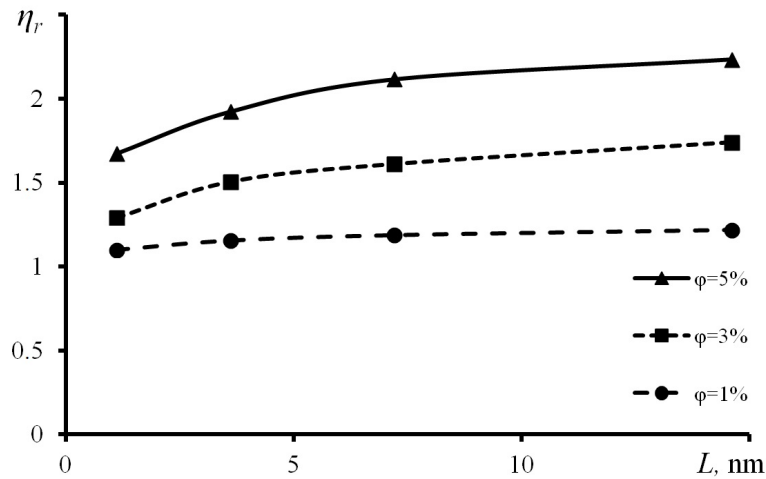


FIG. 2. Dependence of the relative viscosity coefficient of the nanofluid on the CNT length at different volume concentrations φ

Thus, it is shown that the viscosity of NFs with CNTs is significantly higher than the viscosity of NFs with spherical particles. It's not surprising. For suspensions with solid ellipsoidal particles, the viscosity coefficient was obtained by J.B. Jeffrey [47]. The viscosity coefficient of a dispersed medium increased as the shape of the particles deviated from a spherical configuration. This is expected due to the shorter Brownian rotation time in comparison with the considered hydrodynamic time period. Consequently, the rotation of the particles results in an increase in the effective volume they occupy. The elongated ellipsoid is an effective model for the solid CNT. Later, it was shown in [48] that suspensions comprising ellipsoidal particles should manifest viscoelastic properties. For NFs with SWCNTs, this was revealed experimentally in [17, 18].

NF is a complex dispersed system. Its viscosity is determined by the processes of momentum dissipation in the system. In turn, this dissipation process is determined by various contributions in the viscosity coefficient (see (1) and (2)). Therefore, to understand the mechanisms of momentum dissipation in NFs, it is necessary to analyze the various contributions to the viscosity coefficient (1), (2). Previously, such an analysis was performed for NFs with spherical NPs [49, 50]. Several important facts were revealed. Firstly, it was shown that the contribution of kinetic processes to momentum transport (viscosity) in NFs is insignificant and lower than in the base fluid. This reduction is due to the decrease in the number density of molecules in the NFs compared to the base fluid. The main increase in the viscosity

TABLE 1. Parameter values in formula (4)

$\varphi, \%$	$a(\varphi)$	$b(\varphi)$
1	0.2224	1.6508
3	0.1729	1.2758
5	0.0465	1.0937

coefficient is attributed to nanoparticle–molecule interactions as well as correlations between molecule–molecule and nanoparticle–molecule interactions. Below such an analysis is made for a nanofluid with CNTs.

The microscopic momentum flux tensor (2) for a binary system has the following form

$$\mathbf{J} = \mathbf{J}_k + \mathbf{J}_p, \quad (5)$$

where the kinetic contribution is

$$\mathbf{J}_k = \frac{1}{V} \sum_{\alpha=1}^2 \sum_{i=1}^{N_{\alpha}} m_{\alpha} \mathbf{v}_i \mathbf{v}_i.$$

In turn, the potential contribution consists of two parts

$$\mathbf{J}_p = \mathbf{J}_{p1} + \mathbf{J}_{p2},$$

related to the carrier fluid

$$\mathbf{J}_{p1} = \frac{1}{2V} \sum_{i=1}^{N_1} \sum_{j=1}^{N_1} \mathbf{F}_{ij} \mathbf{r}_{ij} + \frac{1}{2V} \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \mathbf{F}_{ij} \mathbf{r}_{ij}$$

and to the CNTs

$$\mathbf{J}_{p2} = \frac{1}{2V} \sum_{i=1}^{N_2} \sum_{j=1}^{N_2} \mathbf{F}_{ij} \mathbf{r}_{ij} + \frac{1}{2V} \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \mathbf{F}_{ij} \mathbf{r}_{ij}.$$

Accordingly, it is also convenient to divide the viscosity coefficient (1) into several summands

$$\eta = \eta_k + \eta_p + \eta_{kp}, \quad (6)$$

which determine the kinetic contribution

$$\eta_k = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_k(0) : \mathbf{J}_k(t) \rangle dt, \quad (6a)$$

potential contribution

$$\eta_p = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_p(0) : \mathbf{J}_p(t) \rangle dt \quad (6b)$$

and cross kinetic-potential contribution

$$\eta_{kp} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_k(0) : \mathbf{J}_p(t) + \mathbf{J}_p(0) : \mathbf{J}_k(t) \rangle dt. \quad (6c)$$

Further, the potential contribution to the viscosity coefficient can be represented as follows

$$\eta_p = \eta_{p1} + \eta_{p2} + (\eta_{p1p2} + \eta_{p2p1}), \quad (7)$$

where

$$\eta_{p1} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p1}(0) : \mathbf{J}_{p1}(t) \rangle dt, \quad \eta_{p2} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p2}(0) : \mathbf{J}_{p2}(t) \rangle dt, \quad (7a)$$

$$\eta_{p1p2} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p1}(0) : \mathbf{J}_{p2}(t) \rangle dt, \quad \eta_{p2p1} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p2}(0) : \mathbf{J}_{p1}(t) \rangle dt. \quad (7b)$$

The contributions to the viscosity coefficient of pure benzene and NF with CNTs are presented in Table 2. Here, the length of the CNTs is 7.2 nm and their weight concentration is 3 %. The viscosity of NF is 12.9 % greater than that of benzene. This increase is mainly due to the potential contribution, which in turn has increased by 7.7 % due to the rise in the viscosity of the carrier fluid (η_{p1}), and by 5.2 % due to the viscosity of the nanotubes (η_{p2}). The latter term determines

not only the interaction of the nanotubes themselves, but also the cross-interaction of CNTs with the base fluid molecules (see (7a) and (7b)).

The viscosity of fluid is determined by the local destruction of the short-range order within the fluid and the formation of a new order. The contributions of η_{p1} and η_{p2} to the viscosity coefficient (1) encompass direct interactions between the base fluid molecules and CNTs as well as cross-interactions between CNTs and the base fluid molecules. The increase in viscosity should therefore be attributed to a change in the structure of the base fluid in the NF, and the possible formation of a short-range order of the CNT pseudo-fluid. The radial distribution function (RDF) serves as an indicator of the fluid short-range order. The structuring of base fluid molecules around spherical NPs by MD method has been established previously [51, 52]. This structuring is determined by the surface area of NPs at given interaction potential parameters.

Similarly, the structuring of the base fluid molecules near the CNTs also occurs in the NF. Fig. 3 presents a comparison of the RDFs (g_2) of benzene fluid molecules (solid line) and benzene molecules of the NF with 1.1-nm diameter CNTs and 1.45, 3.56, 7.25, and 14.61 nm long. In all cases, the volume concentration of CNTs is 2 %. As the length of the nanotubes increases, the RDF maxima of benzene molecules in the NF and the short-range order extent also increase. At the maximum length of the CNTs, the first maximum of the RDF exceeds the corresponding value for pure benzene more than twice. The second, third, and subsequent maxima increase even more. In addition, the extension of the short-range order in NF with CNTs nearly doubles in comparison with that in pure benzene. The viscosity of the fluid also increases with the growth of the magnitude of the RDF maxima and their number. Structuring of the base fluid molecules around CNTs is exactly one of the main factors influencing the growth of the viscosity of NF. As previously mentioned, the structuring of the molecules depends on the surface area of NPs or CNTs. In paper [29], it was shown that the surface area of CNT is almost always larger or even much larger than the surface area of a spherical NP (at the same CNTs concentration, of course). As a result, the structuring of the base fluid molecules near CNT is significantly greater than near a spherical NP. Therefore the viscosity of the NF with CNTs will be greater than that of the NF with spherical NPs.

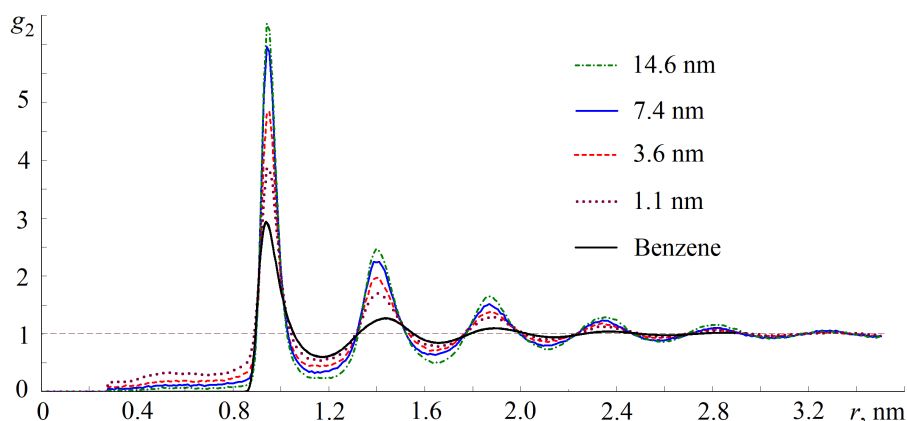


FIG. 3. Radial distribution functions of benzene molecules in benzene and benzene-based nanofluid containing different size CNTs

The analysis of data in Table 2 shows that the contribution made by the term η_{p2} to the viscosity coefficient is rather significant. This, in particular, may indicate the structuring processes of CNT pseudogas. Such structuring can also be studied by analyzing the corresponding RDFs, which are shown in Fig. 4. Here, in all cases, the volume concentration of CNTs is equal to 2 %. The behavior of the RDF strongly depends on the CNT length. At the maximum CNT length, a short-range order from CNTs starts to form in the NF.

In experiments examining the viscosity and rheology of NF with SWCNTs, it was demonstrated that starting from CNT weight concentrations of 0.05 %, the NF exhibits non-Newtonian behavior [7, 17, 18]. This rheological behavior is largely related to the percolation of CNTs within the NF. The formation of a percolation structure of CNTs in the NF is a threshold phenomenon that is dependent on the concentration of CNTs. The corresponding critical concentration is determined by the average distance between CNTs. Once the distance between the CNTs reaches the order of the radius acting of van der Waals forces, percolation begins to form. In the above presented MD computation data percolation was not observed. This is due to two circumstances. Firstly, the concentration of CNTs was insufficient for this purpose, since CNT length is relatively small. The second reason is that the interaction of CNT atoms is determined by the potential (3), whereas in real CNTs, the van der Waals forces acting between them are significantly larger [53, 54].

4. Viscosity of hybrid nanofluids

Analysis of the data from the above MD computations allows concluding in general terms what result should be expected when simulating the viscosity of HNFs. The viscosity of NFs comprising both NPs and CNTs is predominantly

TABLE 2. Contributions to the viscosity coefficient (mPa·s) of benzene and benzene-based nanofluid with CNTs, $w = 0.03$, $\varphi \approx 0.01$

	Benzene	Benzene–CNT
η	0.604	0.6819
η_k	0.0051	0.0056
η_p	0.5942	0.6732
η_{kp}	0.0047	0.0031
η_{p1}	0.5942	0.6412
$\eta_{p2} + \eta_{p1p2} + \eta_{p2p1}$		0.0320

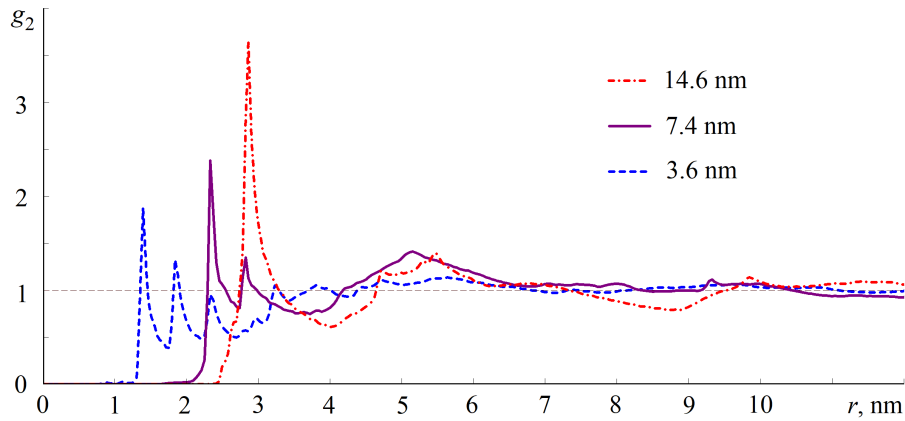


FIG. 4. Radial distribution functions of CNTs of different sizes in benzene-based nanofluid

influenced by the structuring of the base fluid molecules. In HNFs, the molecules of the base fluid are structured around both the NPs and the CNTs. For this reason, at a given volume concentration of NPs and CNTs, the molecules of the base fluid are significantly more structured compared to those in NF with NPs or NF with CNTs at the same volume concentration. Therefore, it is to be expected that the viscosity of the HNFs will be greater than that of the NF with NPs or NF with CNTs. However, this conclusion requires further verification.

The MD simulation data on the viscosity of HNFs with CNTs of length 14.6 nm and copper NPs of diameters equal to 1.4 and 3.2 nm in benzene at temperature $T = 25^\circ\text{C}$ and atmospheric pressure are presented in Fig. 5. The volume concentrations of CNTs φ_{CNT} were 0.5 or 1 %, and the concentration of Cu NPs φ_p ranged from 1 to 5 %. Thus, the simulations provided information on the effects of both CNT and Cu NP concentrations on the viscosity of HNF. Fig. 5 presents the MD simulation data on the dependence of the relative viscosity coefficient of the specified benzene-based HNF on the NP volume concentration at fixed CNTs volume concentration (0.5 or 1 %). The HNF with CNTs at a concentration of 1 % as well as 1.4 nm copper NPs are represented by circle symbols, whereas those with a size of 3.2 nm are depicted by rhombus symbols. Triangle symbols correspond to the CNTs and 1.4 nm copper NPs at a volume concentration of 0.5 %. The presented data indicate that the viscosity of HNF is significantly higher than the viscosity of NF with CNTs (see Fig. 2) and the viscosity of NFs with NPs (see data in [29]). Furthermore, it should be noted that the viscosity of HNF increases with increasing CNT concentration. Finally, the viscosity of HNF depends on the size of the NPs; it is greater the smaller the size of the NPs.

The dependences shown in Fig. 5 are well approximated by the following quadratic function of the effective volume concentration φ_{eff}

$$\eta_r = 1 + c_1\varphi_{\text{eff}} + c_2\varphi_{\text{eff}}^2, \quad (8)$$

where the effective volume concentration is determined by the following relation

$$\varphi_{\text{eff}} = \varphi_p + \varphi_{\text{CNT}}. \quad (9)$$

The constants c_1 and c_2 in formula (8) for the HNFs, presented in Fig. 5, are summarized in Table 3 (here d_p is the NP diameter in nm). The lines in Fig. 5 correspond to the correlation (8).

For a fixed CNT length and concentration, the viscosity of the corresponding HNF is determined by the NP concentration and size. The viscosity of HNF normalized to that of base fluid (benzene) is then be described by the following

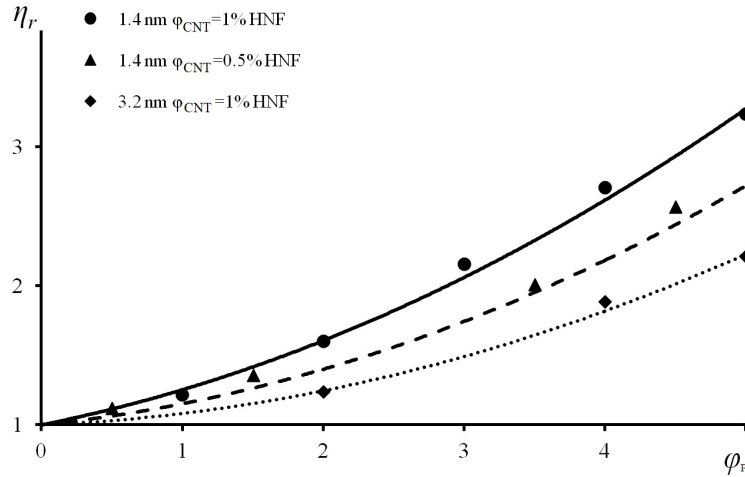


FIG. 5. Dependence of the relative viscosity coefficient of benzene-based hybrid nanofluids on the effective volume concentration of CNTs and nanoparticles

TABLE 3. Parameters of formula (8) for hybrid nanofluids

φ_{CNT}	d_p	c_1	c_2
1 %	1.4	16.169	555.84
1 %	3.2	4.098	408.88
0.5 %	1.4	37.695	104.4

correlation

$$\eta_r = \tilde{a}_0 + \tilde{a}_1 \varphi_p + \tilde{a}_2 \varphi_p^2, \quad (10)$$

For the studied nanofluids, the parameters $\tilde{a}_0$, $\tilde{a}_1$, and $\tilde{a}_2$ are summarized in Table 4.

TABLE 4. Parameters of correlation (11) for benzene-based hybrid nanofluids with CNTs and copper nanoparticles

$\varphi_{\text{CNT}}, \%$	d_p	$\tilde{a}_0$	$\tilde{a}_1$	$\tilde{a}_2$
1	1.4	1.22	28.85	526.82
1	3.2	1.22	7.02	418.20
0.5	1.4	1.12	40.48	70.96

5. Conclusions

In this paper, the MD method was used to simulate the viscosity coefficients of benzene-based NFs with CNTs and HNF with CNTs and copper NPs. In all cases, the dependence of the viscosity of these NFs and HNFs on the concentration of CNTs and NPs, as well as on the morphology of dispersed particles, was studied. The data obtained are systematically analyzed. The findings allow drawing the following conclusions.

- The viscosity of all the studied NFs is significantly higher than that of the base fluid and conventional coarse-dispersed fluids [7, 46].
- The viscosity coefficient of NF with CNTs at a given volume concentration increases with increasing their length (aspect ratio).
- The viscosity coefficient of NF with CNTs at fixed volume concentrations is higher than those for NF with spherical nanoparticles.
- One of the principal factors responsible for the observed increase in the viscosity of NF in comparison with the corresponding value for the base fluid is the structuring of the base fluid molecules near the NPs or CNTs. This structuring is determined by the parameters of the interaction potential between the base fluid molecules and the atoms of the NPs or CNTs, as well as their surface area.

- At equal concentrations, the viscosity of HNF significantly exceeds the viscosity of NF with NPs or CNTs and increases with decreasing in nanoparticle size. The obtained MD data fundamentally allow us to qualitatively predict the viscosity of HNFs with CNTs and NPs.
- The influence of the NPs and CNTs concentrations on the HNF viscosity can be described by the effective volume concentration (9). In this case the dependence of the HNFs on the effective concentration has the ordinary quadratic form (8).

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