

Molecular dynamics study of nanofluids viscosity with carbon tubes

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ABSTRACT The purpose of this paper is molecular dynamics simulation of viscosity of benzene-based nanofluids with carbon nanotubes, and carbon or copper nanoparticles. The nanotubes diameter and lengths were 1.1 nm and 1.1, 3.5, 7.2, 14.6 nm, respectively. The size of spherical nanoparticle was 1.39, 2.5, and 3.2 nm. The viscosity is calculated using the fluctuation-dissipation theorem (the Green–Kubo formula). It was shown that the viscosity coefficient of all the studied nanofluids with carbon nanotubes increases with their concentration and length. This increase is significantly higher than predicted by the corresponding theories for coarse dispersed fluids. At given weight concentrations, the viscosity coefficient of nanofluids with carbon nanotubes is higher than that of nanofluids with spherical particles. The increase in viscosity of nanofluids compared to that of the base fluid is explained by the structuring of the base fluid molecules in the vicinity of nanoparticles or carbon nanotubes.

KEYWORDS viscosity, molecular dynamics method, nanofluid, nanoparticles, carbon nanotubes

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1. Introduction

Nanofluids have unique properties that have been studied for over 25 years. They are currently being used or targeted on for use in various biomedical, cosmetic, and thermophysical technologies, as well as in the creation of advanced materials, in tribology, pharmacology, etc. [1–7]. Since the viscosity is a crucial factor for the potential applications of nanofluids, it has been extensively investigated. It has been experimentally established that the viscosity of nanofluids is significantly higher than that of conventional coarse dispersed fluids [1, 8–11]. Additionally, the viscosity of nanofluids depends not only on the concentration but also on size and material of the nanoparticles [1, 8–12]. With increasing the size of nanoparticles, the viscosity of the nanofluid decreases. An increase in temperature of the nanofluid results in a decrease in viscosity. This decrease is determined by the corresponding viscosity dependence of the base fluid, especially at low particle concentrations [13–16].

The dependence on both size and material was first established by the molecular dynamics (MD) method and later confirmed experimentally [17–20]. In general, the MD method has been widely used to investigate the viscosity of nanofluids. The relevant bibliography for nanofluids with conventional spherical particles can be found in the reviews [20, 21]. In addition to the fact that the use of the MD method has revealed new factors affecting the viscosity of nanofluids, it is absolutely indispensable when studying the corresponding mechanisms. It is due to this method that it was revealed that the greatest contribution to momentum transfer in nanofluids is related to the interaction of fluid molecules with nanoparticles [18, 20] and the structuring of the base fluid [20, 22].

Today, dispersed fluids with carbon nanotubes (CNTs) are also referred to as nanofluids. The viscosity and rheology of nanofluids with CNTs have been studied for about twenty years. However, studying such nanofluids is complicated due to the fact that CNTs can be single-walled (SWCNTs) or multi-walled (MWCNTs), which results in different their rheology and viscosity. This has been systematically shown in a recent work [23]. CNTs are unique particles, their diameters ranging from 1 – 2 nm for SWCNTs to 100 nm for MWCNTs. Their lengths also vary, with SWCNTs typically around 4 – 5 μm and MWCNTs reaching tens of micrometers. Strictly speaking, one of the CNT sizes turns out to be significantly larger than the limit size of spherical nanoparticles (100 nm). Such a complex morphology of CNTs makes them a difficult object for MD modeling. So far, only a few papers have been published.

The viscosity of a water-based nanofluid with 0.95 nm diameter of SWCNTs was simulated in one of the first papers [24]. The interaction of carbon atoms in CNTs was described using the Tersoff potential and their interaction with water molecules was described by the Lennard–Jones potential. A single CNT was used in the simulation cell, so that

the possible effect of CNT interaction on the viscosity of the nanofluid was excluded. Another disadvantage of this paper was that the increase in CNT concentration from 0.125 to 1 % was achieved simply by the corresponding elongation of the nanotubes. The length of the CNTs varied from 0.22 to 1.78 nm. However, it is clear that in this case, the viscosity of completely different nanofluids is actually compared and it is simply impossible to draw a meaningful conclusion about the dependence of the viscosity of a nanofluid with given CNTs on their concentration. Here a nanofluid simply with nanoparticles of a non-spherical shape, and of a very small size is actually considered. However, the authors also analyzed the effect of temperature on the viscosity of these nanofluids. The calculations seem reasonable when the CNT concentration is constant. The study revealed that the viscosity of nanofluids decreases monotonically at a fixed CNT concentration (i.e., at a fixed CNT length). At the same time, it is indicated that the relative viscosity (the ratio of the viscosity of nanofluid to the viscosity of the base fluid) increases with increasing temperature, starting from the nanotube length of 0.88 nm, and this growth is greater the longer the CNTs. In contrast, the relative viscosity of nanofluids with particles of shorter length decreases with increasing temperature.

In another series of calculations, the length of the tubes was fixed and equal to 2.5 nm (the volume concentration was 0.734 %), but the diameter varied from 1.11 to 1.59 nm. The results have shown that the variation in diameter had almost no noticeable impact on the viscosity of the studied nanofluids.

In the following paper of the same authors [25], viscosity calculations of similar nanofluids were performed. The diameter of CNTs was 0.951 nm, and their length varied from 0.22 to 1.3 nm, allowing for CNT concentrations to be varied in the range of 0.125 – 0.734 %. The results obtained were qualitatively the same as in the previous work. It should be noted that according to the authors, the viscosity of the nanofluids is significantly higher than that predicted by classical theories [26–28].

In another set of studies [29, 30], nanofluids were simulated using water and armchair-type (6, 6) CNTs with a length of 3 nm at temperature range of 298 – 313 K. The volume concentration of CNTs was varied from 0.557 to 3 %. The simulation cell contained only one CNT again. The results have shown that the viscosity of nanofluids was significantly higher than that of the base fluid and increased with increasing CNT concentration. It was noted that the viscosity of the nanofluid decreased as the temperature increased. It is worth noting that the viscosity of the nanofluid was significantly higher than that predicted by classical theories. In this case, a comparison was made with Brinkman's theory [27]. Finally, this work proposes a correlation for the viscosity coefficient based on temperature and CNT concentration, derived from numerical analysis of MD data. However, caution should be exercised when interpreting the obtained correlation for two reasons. Firstly, it is difficult to classify CNTs as proper nanotubes due to their length being of the same order as their diameter. Secondly, the viscosity coefficient, calculated using Green–Kubo formulas, has not reached the plateau values.

To conclude this forcedly very brief review of MD simulation of viscosity of nanofluids with CNTs it should be noted that still a number of fundamental issues remain unexplained. This concerns the following issues. (i) How does the viscosity of nanofluids vary with the aspect ratio (length-to-diameter ratio) of CNTs? (ii) How does the nanofluid viscosity depend on CNTs length? (iii) How does the viscosity of nanofluids with CNTs depend on their concentration? (iv) How does the viscosity of nanofluids with CNTs relate to that of conventional spherical particles? This article is devoted to answering these questions.

The immediate purpose of this paper is MD modeling of the viscosity coefficient of several benzene-based nanofluids with CNTs and carbon or copper nanoparticles. Benzene was chosen as the base fluid due to the hydrophobic nature of CNTs, which makes it impossible to create a water-based nanofluid without the use of any surfactants. From this viewpoint, the above referred data [24, 25, 29, 30], which use water as the base fluid in their calculations are model-based and cannot accurately simulate a real nanofluid. Alternately, carbon nanotubes (CNTs) are lyophilic to benzene and various alcohols (isopropanol, ethylene glycol, and etc).

Armchair-type CNTs with chirality (8, 8) were used as nanotubes, their diameter was 1.1 nm and lengths were 1.1, 3.5, 7.2, and 14.6 nm. Respectively, the CNTs were composed of 160, 480, 960, and 1920 carbon atoms. The number of benzene molecules in the simulation cell varied from 6700 to 38000, so that the weight concentrations of CNTs were 3, 9, and 15 %, which roughly corresponded to the volume concentrations of 1, 3, and 5 %. The number of CNTs in the calculations varied from 4 to 48, and the number of nanoparticles varied from 6 to 24.

To compare, the viscosity of nanofluids with spherical carbon and copper particles with diameters of 1.39, 2.5, and 3.2 nm was studied simultaneously. The mass of the carbon nanoparticles was equal to the mass of the corresponding CNTs. Given this, the size of the nanoparticles was determined. Thus, the indicated diameters of carbon nanoparticles corresponded to CNT lengths of 1.1, 7.2, and 14.6 nm. The weight concentrations of carbon particles were equal to those of CNTs. The volume concentrations of copper and carbon nanoparticles coincided and were equal to 1.16, 3.5, and 5.8 %.

2. Simulation technique

The simulation of nanofluid viscosity was performed based on MD method [31] using free LAMMPS package [32]. The shear viscosity coefficient was determined by the fluctuation-dissipation theorem, known in the literature as the

Green-Kubo formula [33–35]:

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

where the microscopic stress tensor for the considered binary mixture has the following form

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

Here the index $\alpha = 1$ refers to the carrier fluid molecules, and 2 refers to the CNT atoms or nanoparticles, m_i is the mass of the corresponding particle (molecule or nanoparticle), V is the volume of the system, T is the temperature of the medium, τ_p is the time to reach the plateau value, \mathbf{F}_{ij} is the force acting on the particle (molecule or nanoparticle), \mathbf{r}_{ij} is the radius-vector between the centers of the interacting particles, and k_B is the Boltzmann constant. N_1 and N_2 are the number of molecules of the carrier fluid and atoms of the nanotubes or nanoparticles, respectively. The angular brackets in (1) denote averaging over the equilibrium ensemble.

The simulation was conducted in cubic cells with periodic boundary conditions. To determine the viscosity coefficient, the simulated system needed to be brought to an equilibrium state due to the fluctuation-dissipation theorem (1), according to which the coefficient is determined by the equilibrium thermal fluctuations of the stress tensor. To investigate a nanofluid with CNTs, the following procedure was followed: initially, benzene molecules were uniformly placed in the simulation cell, based on the given density $\rho_f = 0.8765 \text{ g}\cdot\text{cm}^{-3}$ (corresponding to atmospheric pressure and a temperature of 25 °C), except for the volume occupied by CNTs. The initial velocities of molecules were set according to the Maxwell distribution at a given temperature. The calculation began after a relaxation period of 1 – 1.5 ns, during which the entire system reached equilibrium. The initial state of the nanofluid with nanoparticles was also reached using the same method.

To calculate the viscosity coefficient (1) using MD method, it is necessary to first calculate the corresponding two-time correlation function χ_η . This calculation requires information about all dynamic variables of the system at successive instants, for which the corresponding system of Newton's equations is solved sequentially. Newton's equations were integrated using the Verlet scheme. The NPT Nose–Hoover thermostat [36,37] was used to maintain atmospheric pressure and a temperature of 25 °C. The interaction between benzene and carbon molecules was determined using the Lennard–Jones potential

$$\Phi_{LJ}(r) = 4\varepsilon_{ij} \left[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6 \right], \quad (2)$$

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 potential parameters (1) for benzene molecules are $\sigma_1 = 0.5034 \text{ nm}$, $\varepsilon_1/k_B = 544.3 \text{ K}$, for carbon atoms – $\sigma_2 = 3.4157 \text{ \AA}$, $\varepsilon_2/k_B = 27.70 \text{ K}$, and for copper atoms – $\sigma_2 = 2.2268 \text{ \AA}$, $\varepsilon_2/k_B = 2255.3 \text{ K}$. The density of carbon was taken equal to $\rho_G = 2267 \text{ kg}\cdot\text{m}^{-3}$, and that of copper was $\rho_{Cu} = 7998 \text{ kg}\cdot\text{m}^{-3}$. The interaction potential parameters (2) between the carrier fluid molecule and carbon atoms of CNT or nanoparticle were calculated using simple combination relations [38]: $\sigma_{12} = \sqrt{\sigma_1 \sigma_2}$, $\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$. Since the potential (2) has an infinite action radius, it needs to be cut-off in the simulation process, the cut-off radius was $2.5 \sigma_1$. The CNT was simulated by a set of carbon atoms interacting using the AIREBO potential [39].

The interaction of benzene molecules with carbon or copper nanoparticles was described by the Rudyak–Krasnolutskiï potential [40,41]:

$$\Psi(r) = \Psi_9(r) - \Psi_3(r), \quad (3)$$

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

where $i = 9, 3$, $a_9 = 9/8$, $a_3 = 3/2$, $C_9 = (4\pi\varepsilon_{12}\sigma_{12}^{12})/45V_p$, $C_3 = (2\pi\varepsilon_{12}\sigma_{12}^6)/3V_p$, $V_p^{-1} = \rho_p/m_p$. Here ρ_p is the density of the nanoparticle material, m_p is the mass of an atom (molecule) of the nanoparticle material, R is the nanoparticle radius, σ_{ij} , ε_{ij} are the parameters of the potential (2) between the carrier fluid molecule and the nanoparticle atom.

The Rudyak–Krasnolutskiï–Ivanov potential [42] is used to describe the interaction between carbon or copper nanoparticles. This potential has the following form:

$$U(r, R) = U_7(r, R) - U_1(r, R), \quad (4)$$

$$\begin{aligned}
U_7(r, R) &= \frac{\pi^2 \varepsilon_2 \sigma_2^{12}}{315 V_p^2} \left\{ \frac{R^2}{r} \left[\frac{1}{(r-2R)^7} + \frac{2}{r^7} + \frac{1}{(r+2R)^7} \right] - \right. \\
&\quad \left. - \frac{R}{3r} \left[\frac{1}{(r-2R)^6} - \frac{1}{(r+2R)^6} \right] - \frac{1}{30r} \left[\frac{1}{(r-2R)^5} - \frac{2}{r^5} + \frac{1}{(r+2R)^5} \right] \right\}, \\
U_1(r, R) &= \frac{2\pi^2 \varepsilon_2 \sigma_2^6}{3 V_p^2} \left[\ln \left(\frac{r^2 - 4R^2}{r^2} \right) + 2R^2 \left(\frac{1}{r^2 - 4R^2} + \frac{1}{r^2} \right) \right].
\end{aligned}$$

Here R is the radius of nanoparticles, σ_2 and ε_2 are parameters of the Lennard–Jones potential (2) of the interaction between nanoparticle atoms.

The potential (3) was constructed based on the assumption that the interaction between the carrier fluid molecules and nanoparticle atoms, as well as between nanoparticle atoms themselves, can be described by potentials (2) with parameters σ_{12} , ε_{12} , and σ_2 , ε_2 , respectively. The adequacy of this potential was experimentally verified by simulating the diffusion of nanoparticles in nitrogen [43]. Potential (4) was constructed in a similar manner. Later, both potentials were used to simulate various transport coefficients in nanofluids [20].

For potential (3), the cut-off radius was $(R + b\sigma_{12})$. The value of parameter b was selected to ensure that the force exerted on the molecule from the nanoparticle was equal to the interaction force between two molecules at the cut-off radius for potential (1). The parameter b is dependent on the nanoparticle size and material, as well as the properties of the carrier fluid molecules. For instance, for 1.39 nm diameter carbon nanoparticles in benzene, $b = 3.0$, while for 3.2 nm diameter nanoparticles, b equals $b = 3.34$. The nanoparticle potential (4) was cut off at a distance of two particle diameters between the centers of the nanoparticles.

Because of the local instability and mixing of the system's phase trajectories during MD simulation [44–46], the obtained data must be averaged over an ensemble of independently constructed phase trajectories. In this paper, averaging was performed over at least 1000 independent phase trajectories.

In the simulation, the dependence of the nanofluid viscosity on the weight concentration w of CNTs or nanoparticles was studied. The relationship between weight concentration and volume concentration ϕ is determined by the following equation

$$\phi = w [w + (1 - w)\rho_p/\rho_f]^{-1}, \quad (5)$$

where ρ_f and ρ_p are mass densities of fluid and nanoparticles, respectively.

3. Simulation of the nanofluid viscosity

The nanofluids studied in this paper were prepared using benzene. Therefore, the first step was to simulate the viscosity of benzene and compare it with experimental data. It was found that at atmospheric pressure and a temperature of 25 °C, the calculated benzene viscosity coefficient was 0.6 mPa·s, which closely matched the measured value [47].

The viscosity coefficient of nanofluid with CNTs was calculated by varying both their length and concentration. In all cases, the viscosity coefficient $\eta(t)$ (1) was considered calculated when it reached the plateau value. An example of this is shown in Fig. 1, which displays the evolution of the viscosity coefficient of a nanofluid with CNTs with length of 1.1 nm at a nanotube weight concentration of 3 %. The simulation cell contained 9 CNTs and 7184 benzene molecules. The graph displays the benzene viscosity coefficient as a dashed line and the plateau value of the nanofluid viscosity coefficient as a solid line. Time is measured in femtoseconds, and the plateau is reached in approximately 30 picoseconds. The calculated viscosity coefficient of the nanofluid is 9.5 % higher than that of the base fluid (benzene).

The dependence of the relative viscosity coefficient $\eta_r = \eta/\eta_{bf}$ (where η_{bf} is the viscosity coefficient of benzene) of nanofluids with CNTs of different lengths on their volume concentration is shown in Fig. 2. The nanotubes have lengths of 1.1, 3.5, 7.2, and 14.6 nm. The corresponding data and solid curves are depicted from bottom to top, and the dashed line corresponds to Batchelor's theory [28]. Based on the obtained data, several conclusions can be drawn. The first conclusion is that the viscosity coefficient of all nanofluids is significantly higher than that of coarse dispersed fluids, as concluded particularly in [28].

The second conclusion is that the viscosity coefficient increases with the length of CNTs at a given weight concentration. More precisely, viscosity depends on the aspect ratio of CNTs, since in this case the diameter of all CNTs was the same. The viscosity of nanofluids with ordinary spherical particles also depends on their radius, and it is the greater the smaller the size of the nanoparticles. This fact was established both experimentally [1, 8, 9] and by the MD simulation [17, 20]. Such dependence is primarily determined by the structuring of the base fluid in the vicinity of the nanoparticles [20]. This structuring is determined by the surface area of the nanoparticles at given values of the interaction potential parameters. Since the surface area of CNTs of the same diameter is proportional to their length, the viscosities of nanofluids with CNTs will be increased proportionally to the length of CNT. For suspensions with solid ellipsoidal particles, the corresponding viscosity coefficient was obtained by G. B. Jeffrey [48]. The viscosity coefficient of a dispersed medium grows as the particle shape deviates from spherical. This is expected due to the shorter Brownian rotation time compared to the hydrodynamic times considered. Therefore, particle rotation leads to an increase in the effective volume they occupy. The prolate spheroidal ellipsoid models a solid CNT quite well. Later, in [49] it was shown that

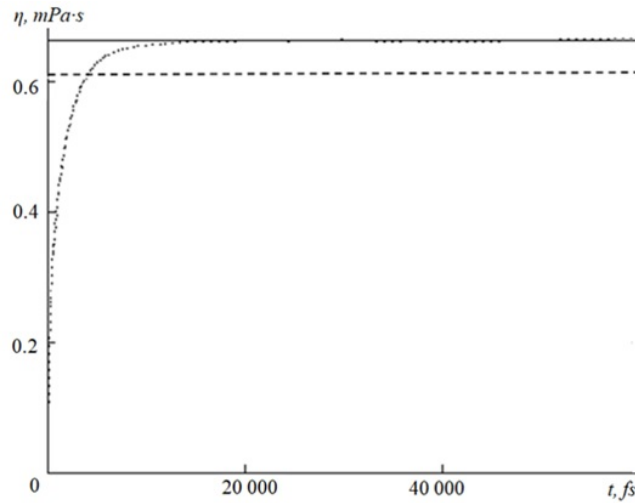


FIG. 1. Evolution of the viscosity coefficient of benzene-based nanofluid with CNTs

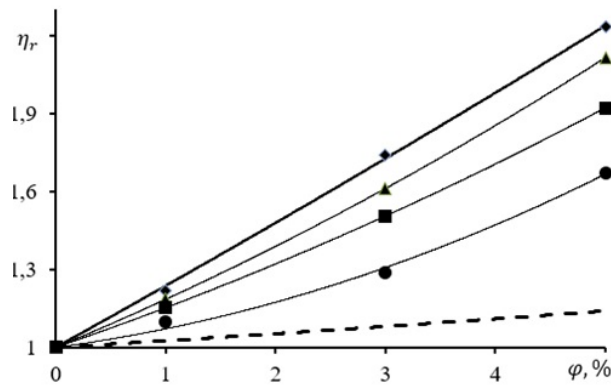


FIG. 2. Dependence of relative viscosity coefficient of nanofluids on CNT volume concentration

suspensions with ellipsoidal particles should have viscoelastic properties. For nanofluids with CNTs, this was established experimentally in [23].

The third conclusion is that the dependence of the viscosity coefficient of both coarse dispersed fluids and nanofluids with spherical particles on the volume concentration of particles is described by the square law dependence [9, 20]:

$$\eta_r = 1 + a_1\phi + a_2\phi^2. \quad (6)$$

The volume concentration dependence of the viscosity coefficient of the CNT nanofluids is also described by this formula. The coefficients in this formula are dependent on the length of the CNT and are presented in Table 1. The solid lines in Fig. 2 correspond to the dependences (6).

TABLE 1. Coefficients in formula (6) for benzene-based nanofluids with CNTs

L , nm	1.1	3.6	7.4	14.6
a_1	7.38	16.36	19.59	24.36
a_2	144.23	38.39	45.14	11.27

CNTs have a complex morphology and differ significantly from ordinary spherical nanoparticles. Comparing the viscosity of the both types of nanofluids is crucial. Moreover, this is of independent interest due to the active investigation of thermophysical properties of hybrid nanofluids, in which both CNTs and nanoparticles act as dispersed elements (see, for example, [50, 51] and references therein). For comparison, the viscosity of benzene-based nanofluids containing carbon and copper particles have been calculated. In all cases, the viscosity of these nanofluids was described by the square dependence (6). The corresponding data are summarized in Table 2 (d – is the diameter of nanoparticles). The viscosity of the nanofluids increased as the nanoparticle size decreased, consistent with both experimental data and MD

simulations [1, 8–12]. The comparison of the obtained data is presented in Fig. 3. Here, dark points indicate nanofluids with copper particles, while light points indicate those with carbon particles. In all cases, the size of nanoparticles increases from bottom to top. The viscosity of both nanofluids increases as the nanoparticle size decreases. Additionally, the nanofluid with copper particles has higher viscosity than the one with carbon particles.

TABLE 2. Coefficients in formula (6) for benzene-based nanofluids with CNTs

d , nm	1.4, Cu	2.6, Cu	3.2, Cu	1.4, C	2.6, C	3.2, C
a_1	8.78	4.76	3.92	5.52	4.02	3.40
a_2	573.7	469.8	241.3	134.0	23.2	11.97

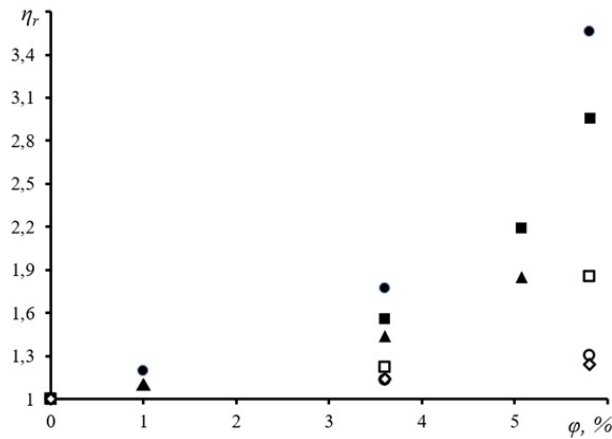


FIG. 3. Dependence of viscosity of benzene-based nanofluids with carbon and copper nanoparticles on their volume concentration

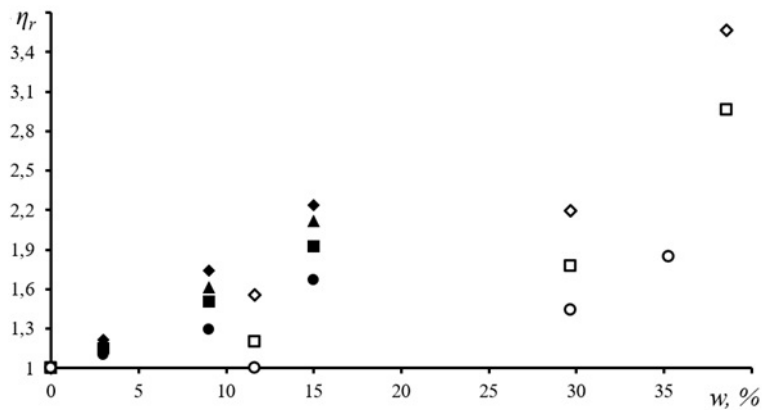


FIG. 4. Comparison of relative viscosity coefficients of nanofluids with CNTs, carbon and copper nanoparticles depending on weight concentration

Nanofluids are typically prepared using a two-step method [1, 8]. First, an appropriate powder of carbon nanotubes (CNTs) or nanoparticles is added to the base fluid to achieve a desired weight concentration. It is important to note that the density of SWCNTs is typically much lower (1.8 g/sm^3) than that of metallic particles. For instance, copper has a density about four times greater. As a general rule, the weight concentration of nanoparticles is typically much higher than that of the corresponding CNT concentrations, even if their volume concentrations are comparable or equal. From this standpoint, it is useful to compare the dependence of viscosity of nanofluids with CNTs and copper particles on weight concentration. Such a comparison is presented in Fig. 4. Here, the dark points correspond to CNTs with lengths of 1.1, 3.6, 7.2 and 14.6 nm (from bottom to top), and the light points correspond to copper nanoparticles with diameters of 1.4, 2.6 and 3.6 nm (from bottom to top). As shown in Fig. 4, the nanofluid with CNTs has higher viscosity than the nanofluid with copper particles at the same weight concentrations. However, while comparing the viscosity at the same volume concentrations, the viscosity of nanofluid with copper particles is higher (see Figs. 3 and 2).

4. Results and discussion

The simulation data, obtained based on MD method require some comments. The viscosity of nanofluids, as well as basic fluids, is determined by the fluctuation-dissipation theorem (1). This theorem states that the momentum redistribution in the system is determined by the dynamics of thermal equilibrium fluctuations of the microscopic stress tensor. The dynamics of the stress tensor and the evolution of the two-time correlation function χ_{η} depend on the structure of the fluid's short-range order. The dissipation of momentum in the fluid is associated with a permanent local rearrangement of the short-range order structure. In nanofluids, the molecules of the base fluid are structured near the nanoparticles. The nature of this structuring is well represented by the radial distribution function (RDF), which determines the average local density of the base fluid molecules around each nanoparticle. As an example, Fig. 5 demonstrates the radial distribution functions of benzene molecules in the vicinity of carbon nanoparticles. The dashed line represents the RDF of pure benzene molecules, while the dotted, dash-dotted, and solid lines correspond to the benzene molecules in the nanofluids surrounding carbon nanoparticles with diameters of 1.4, 2.6, and 3.2 nm, respectively. In all cases, the volume concentration of nanoparticles was the same and equal to 5 %.

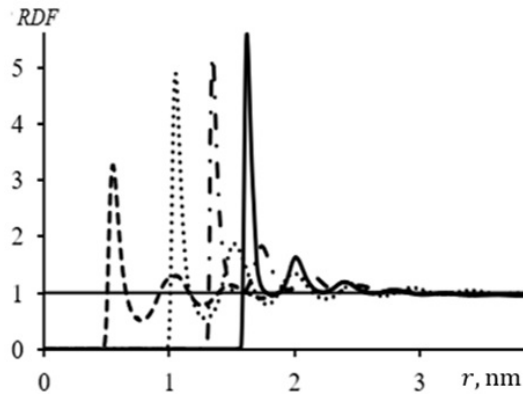


FIG. 5. Radial distribution functions of pure benzene molecules (dashed line) and benzene molecules in nanofluids around graphite nanoparticles with diameters of 1.4 nm (dotted line), 2.6 nm (dash-dotted line), and 3.2 nm (solid line)

The RDFs of benzene molecules surrounding the nanoparticles have significantly higher maxima compared to the corresponding values of the pure liquid. This indicates greater ordering of benzene molecules. As the molecule diameter increases, the degree of ordering of the molecules around the nanoparticles slightly increases, which is due to the decrease in their surface curvature. This effect is observed for particle sizes up to approximately 10 nm, and further the character of the wall layer of molecules remains practically unchanged. However, the viscosity of the nanofluid is not only determined by the magnitude of these maxima, but also by the total number of structured fragments of the base fluid. The total volume of structured regions in the base fluid molecules decreases as nanoparticle size increases at a given volume concentration.

Thus, the increase in viscosity of the nanofluid is due to the sharp intensification of the short-range order of the base fluid molecules. The structuring of the based-fluid molecules is proportional to the surface area of the nanoparticles. The ratio of the surface area of a spherical particle to its volume is inversely proportional to the radius of the particle. Therefore, for given nanoparticle volume concentration, the structuring of the base fluid will be the more effective the smaller the particle radius. Therefore the viscosity of nanofluids with spherical particles will increase with decreasing nanoparticle size.

The structuring of the base fluid molecules also occurs in nanofluids containing CNTs. The surface area of CNTs increases proportionally with their length, resulting in an increase in viscosity of the nanofluid as the length of the CNTs increases.

The ratio of the surface area S_{sp} of a spherical nanoparticle of radius R to that of a CNT S_{cnt} of radius R_{cnt} and length L is given by the relation

$$\frac{S_{sp}}{S_{cnt}} = \frac{2R^2}{R_{cnt}^2 + R_{cnt}L}. \quad (7)$$

Here the following situations are possible: $R \sim R_{cnt}$. This ratio for SWCNTs is fulfilled if the diameter of nanoparticles does not exceed 1 – 3 nm, that is, the spherical particles are very small. In this case, $S_{sp}/S_{cnt} \sim R/L \ll 1$. The viscosity of nanofluids with spherical particles will be smaller than that of nanofluids with CNTs, and only for the smallest CNTs ($L \sim R$) will it be almost the same in both cases. This is confirmed by the data presented in Figs. 2 and 3.

For large SWCNT particles the condition $R > R_{cnt} \ll L$ is met. In this case,

$$\frac{S_{sp}}{S_{cnt}} \sim \frac{R^2}{R_{cnt}L} < 1.$$

Again, the viscosity of nanofluid with CNTs will be higher than that of nanofluid with spherical particles. It is easy to see that these two cases exhaust all possible situations for nanofluids with SWCNTs.

5. Conclusions

In this paper, the viscosity coefficient of benzene-based nanofluids with SWCNTs has been simulated by the MD method. The dependence of the viscosity coefficient of the concentration of SWCNTs and their length was investigated. Simultaneously, the viscosity coefficients of nanofluids with spherical carbon and copper particles were calculated. All the obtained data were systematically compared and it is shown that:

- The viscosity coefficient of all studied nanofluids with SWCNTs increases with their concentration. This increase is significantly higher than predicted by the corresponding theories for coarse dispersed fluids.
- At given concentration, the viscosity coefficient of nanofluids with SWCNTs increases with their length (aspect ratio).
- At given weight concentrations, the viscosity coefficient of nanofluids with SWCNTs is higher than that of nanofluids with spherical particles.
- At the same volume concentrations, the viscosity coefficient of nanofluid with copper particles is higher than that of nanofluid with carbon particles.
- One of the main reasons for the increase in viscosity of nanofluids compared to that of the base fluid is the structuring of the base fluid molecules in the vicinity of nanoparticles or CNTs. This structuring is determined by the parameters of the interaction potential between the molecules of the base fluid and atoms of nanoparticles or CNTs and their surface area.

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