Experimental study and molecular dynamics simulation of carbon nanotubes diffusion

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Abstract. The diffusion of single-walled carbon nanotubes was studied experimentally and by the molecular dynamics method. The experiments used the dynamic light scattering method. Distributions and average values of diffusion coefficients of molecules of surfactants and nanotubes in nanofluids based on water were obtained. It was found that these distributions, even at low concentrations of nanotubes, can have two maxima corresponding to tubes of different sizes. The effect of centrifugation on the size distribution of nanotubes has been studied. The diffusion of one-dimensional and three-dimensional models of nanotubes in water has been studied by the molecular dynamics method. The velocity autocorrelation functions of nanotubes of different lengths have been calculated. The presence of a negative region of these functions for small nanotubes has been established. The dependencies of the diffusion coefficient on the length are determined for both models used.

1. Introduction
In the last twenty years, along with conventional nanofluids (with spherical nanoparticles), the properties of nanofluids with carbon nanotubes (CNTs) have also been actively studied. Depending on the manufacturing technology, CNTs can be single-walled (SWCNT) and multi-walled (MWCNT). The characteristics of CNTs are unique. They combine high strength and high elasticity. CNTs can be conductive or have semiconducting properties; their thermal conductivity reaches 6000 W/(m·K). Already today, CNTs are actively used in a variety of applications: in electronics and design of materials with unique properties, new types of filters, supercapacitors, batteries, sensors of various types, etc. (see, for example, [1–3] and the literature cited there). As in the case of conventional nanofluids, it was assumed that nanofluids with CNTs would find application in various thermal engineering applications. However, it turned out later that the possible range of their use is much wider [4, 5]. In addition, it should be noted that practically all possible applications of CNTs require the preliminary creation of the corresponding nanofluids with their detailed characterization.

Studies of nanofluids with CNTs have been carried out for more than twenty years. Thermal conductivity and viscosity were mainly studied [6, 7]. Until now, there are practically no experimental studies of the diffusion of CNTs. There are two works [8, 9], where the CNTs diffusion was studied by means of single-molecule fluorescence microscopy. This was done for some medical purposes, in particular, the penetration of nanoparticles into living organs for the delivery of drugs to areas affected...
by cancer cells was studied in the latest paper. It was shown that the diffusion of CNTs proceeds faster than the diffusion of spherical particles with the same effective diameters. However, the values of the diffusion coefficients obtained in these works differed significantly. The first task of this work was to experimentally study the diffusion of SWCNTs in liquids.

The lack of experimental information stimulates the simulation of CNT diffusion by the molecular dynamics (MD) method. The complexity of such simulation is quite obvious, since, for example, the diameter of SWCNTs is 1–2 nanometers, and their length varies from hundreds of nanometers to micrometers. MD simulation of SWCNT diffusion in water, which is a typical base liquid, is the second task of this work.

2. Experimental study of SWCNT diffusion

The diffusion of SWCNTs produced by the OCSiAl company (Novosibirsk) was studied experimentally. The SWCNT diameter was 1.6 ± 0.4 nm, and their length exceeded 4 μm. Deionized water (W) was used as the primary base fluid, and two surfactants were used: anionic sodium dodecylbenzenesulfate (SDBS), CH₃(CH₂)₁₁C₆H₄SO₃Na, and non-ionic polyvinylpyrrolidone (PVP), (C₆Н₉NО)n. Thus, two base fluids were considered: W+PVP and W+SDBS. The mass concentration of SWCNTs varied from 10⁻²% to 10⁻⁵%, the surfactant concentration was either equal to the concentration of CNTs or was twice as high.

The diffusion of CNTs in base liquids was studied by the dynamic light scattering (DLS) method. A Malvern Zetasizer ZSP was used. For measurements, 1 ml samples of nanofluid diluted to the required CNT concentration were thermostated at a temperature of 25°C. Several measurements were made with each sample, and then the results were averaged. When implementing the DLS method, a transparent cell with nanofluid is irradiated with a laser. The scattered by CNT light from the laser beam is recorded by a detector. Due to the Brownian motion of nanotubes, local fluctuations in the intensity of the reflected light arise. By sequentially measuring the intensity of the reflected light, one can then calculate the corresponding two-time autocorrelation function and determine its relaxation time. Using then this time and the fluctuation-dissipation theorem, we can further determine the diffusion coefficient $D$.

![Figure 1. Distribution (%) of the diffusion coefficient (micron²/s) of SDBS molecules in an aqueous solution (a) and SWCNTs in the base liquid W+SDBS](image)

The base fluids used in experiments are quite complex and include surfactants with large molecules. The presence of such molecules should be recorded during the measurement. Therefore, the first task was to measure the diffusion coefficient of the surfactant molecules. A typical example of the obtained diffusion distribution of SDBS molecules at mass concentration equal to 0.2% is shown in figure 1a. A characteristic feature of this dependence is the presence of two significantly distant peaks. This indicates the presence of micelles and polymicelles in the solution.
On the contrary, the distribution of PVP molecules diffusion coefficient in an aqueous solution has only one peak. The corresponding characteristic value of the diffusion coefficient at a molecular concentration of 0.2% is 1.03 μm²/s.

Strictly speaking, when measuring the diffusion coefficient of a dispersed particle, it is assumed that it is the only one. In real experiments, the concentration of particles in the base fluid is always quite finite. Simple estimates show that a fairly accurate value of the SWCNT diffusion coefficient is obtained if their mass concentration does not exceed 10⁻³%. The distribution of the SWCNT diffusion coefficient at this concentration is shown in figure 1b with a dash-dotted line. The distribution has two maxima, which indicates that even at such low concentrations, the length distributions of SWCNTs are inhomogeneous. The second (smaller) maximum corresponds to individual tubes and the diffusion coefficient of these tubes is several times higher. Thus, the maximum value of the diffusion coefficient of CNTs corresponding to the first (larger) maximum is 2.2·10⁻¹² m²/s, and the second maximum is 1.02·10⁻¹² m²/s. Average values are slightly lower.

Naturally, with an increase in the SWCNT concentration, their diffusion coefficient will decrease. In figure 1b, the dashed line corresponds to a concentration of 0.002%, and the dotted line does to 0.01%. At these concentrations, the maximum values of the diffusion coefficient have the corresponding values: 1.2·10⁻¹² m²/s and 0.7·10⁻¹² m²/s. The averages are slightly lower. The latter value is in good agreement (within 10%) with the data of paper [8].

3. Molecular dynamics simulation of CNT diffusion

To study the diffusion of nanotubes by the MD method, two SWCNT models were used: a solid 3D armchair model. The 1D CNT model was a nanoscale solid carbon rod composed of carbon atoms. The distances between neighboring atoms were 0.27 nm. The tube length ranged from 2.43 to 3.51 nm. The 3D armchair solid model more adequately simulates SWCNT. The nanotube diameter was 0.818 nm, and their length varied from 5 to 30 nm.

The interaction of water molecules with each other and with carbon atoms of SWCNTs was determined by the Lennard-Jones potential

\[ \Phi(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^6 - \left( \frac{\sigma}{r} \right)^{12} \right), \]

where \( \sigma \) is the effective diameter of the molecule, \( \varepsilon \) is the depth of the potential well, and \( r \) is the distance between the centers of interacting molecules. The parameters of potential (1) for water molecules are: \( \sigma_1 = 2.9582 \text{ Å}, \ v_1/k_B = 545.4 \text{ K} \) [10]. For carbon atoms, the following potential parameters (6.1) were used: \( \sigma_2 = 3.4157 \text{ Å}, \ v_2/k_B = 27.70 \text{ K} \) [11]. The parameters of the interaction potential (1) of the carrier liquid molecule with the SWCNT atom were calculated using the simplest combination relations: \( \sigma_{12} = \sqrt{\sigma_1 \sigma_2} \). Potentials (1) had a finite interaction radius equal to 2.5 \( \sigma \).

The standard MD method in a cubic cell or in the form of a rectangular parallelepiped with periodic boundary conditions was used. The initial velocities of the molecules were set according to the Maxwell distribution, the CNT at the initial moment of time was stationary, the total momentum of the system was equal to zero. An open LAMMPS package using an NPT ensemble at a temperature \( T = 273 \text{ K} \) and atmospheric pressure was used for simulation. In the calculations, the number of molecules in a cell varied from 20 thousand to 1.6 million. To stabilize the system, a Nose-Hoover thermostat was used [12, 13].

During the simulation, systematic information is obtained on the velocities and coordinates of all molecules and CNT atoms at successive times. Using it, one can calculate all the necessary quantities, including the transfer coefficients by the methods of nonequilibrium statistical mechanics (see, for example, [14]). In particular, the diffusion coefficient of a nanotube can be calculated by integrating its velocity autocorrelation function (VACF) \( \chi_w(t) \)

\[ D = \int_0^t \chi_w(t) dt, \quad \chi_w(t) = \frac{1}{3} \langle v(0) \cdot v(t) \rangle. \]
Here $v$ is the velocity of the center of mass of the CNT, $\tau_p$ is the time necessary to reach the plateau value of the VACF [15], the angle brackets mean averaging.

On the other hand, this coefficient can be determined from the measured mean square displacement of the center of mass of the CNT

$$<R^2(t)> = 6Dt.$$ \hspace{1cm} (3)

Both methods were used in the work. In figure 2a shows the evolution of the 1D CNTs VACF of different lengths. An important feature of these VACFs is the presence of a negative area. Note that the velocity relaxation of the Brownian and larger macroscopic particles in liquids is exponential. CNTs whose VACFs are shown in figure 2a are very small in size and weight. The liquid molecules act on the tube with a force directed in the opposite direction to the tubes movement. The low inertia of the rod leads to the fact that it quickly slows down or even unfolds. The negative area of the VACF describes just such a reversal.

Figure 2b illustrates the time dependence of the diffusion coefficients of 1D CNTs of different lengths. Here, the solid line corresponds to CNTs with a length of 2.43 nm, the dashed line does 2.97 nm, and the dash-dotted line does 3.51 nm. The dashed straight lines show the corresponding plateau values of the diffusion coefficients. At first, the diffusion coefficient increases, but the presence of a negative VACF region leads to its decrease at times exceeding 0.2 picoseconds. The graph takes on a characteristic hilly shape. At times longer than picoseconds, the curves reach plateau values, which correspond to the diffusion coefficients determined by the MD method.

Typical time dependences of the mean square displacement of the center of mass of these CNTs are shown in figure 3. It can be seen that, at sufficiently long times, the graphs are well approximated by a linear function, which makes it possible to use formula (2) as an alternative method for determining the diffusion coefficient. The results obtained by these two methods are in good agreement with each other.
Figure 3. Dependence of the mean square displacement (angstrom$^2$) of carbon rods with a length of 2.97 nm (solid line) and 3.51 nm (dashed line) on time (in picoseconds). Dotted lines correspond to linear time dependences.

Table 1 shows data on the diffusion coefficients of 1D CNTs; here, for comparison, the diffusion coefficient of water molecules is indicated. It can be seen that with an increase in the length of the rod, the value of $D$ decreases.

**TABLE 1.** Diffusion coefficients $D$ (m$^2$/s) of 1D CNTs of various lengths $L$ (nm) and water molecules.

| $L$ (nm) | 2.43 | 2.97 | 3.51 | water molecule |
|---------|------|------|------|----------------|
| $D$ (m$^2$/s) | $9.7 \cdot 10^{-10}$ | $8.7 \cdot 10^{-10}$ | $7.9 \cdot 10^{-10}$ | $2.3 \cdot 10^{-9}$ |

However, small differences in the sizes of the rods do not allow a detailed study of the nature of the dependence of the diffusion coefficient on the size. This was done for the more realistic 3D model described above. The VACF of the center of mass of the 3D armchair model 5 and 10 nanometers in length are shown in figure 4. The first point of the VACF corresponds to the mean square of the velocity; therefore, for shorter and lighter CNTs, it is twice as large. It is important, however, that for CNT with sizes of both 5 and 10 nm, the negative VACF region is completely absent.

Figure 4. Dependence of the VACF (10$^2$ m$^2$/c$^2$) of 5 nm (solid line) and 10 nm (dashed line) 3D SWCNT models in water on time (in picoseconds).

The diffusion coefficients of three-dimensional CNTs are given in table 2. One can see that with an increase in the length of a nanotube, its diffusion coefficient monotonically decreases and changes from $1.7 \cdot 10^{-10}$ m$^2$/s for 5 nm CNT to $0.5 \cdot 10^{-10}$ for 32 nm CNT.

**TABLE 2.** Diffusion coefficients $D$ (m$^2$/s) of 3D CNTs of various lengths $L$ (nm)

| $L$ (nm) | 5.254 | 10.65 | 21.442 | 32.23 |
|---------|-------|-------|--------|-------|
| $D$ (m$^2$/s) | $1.698 \cdot 10^{-10}$ | $1.212 \cdot 10^{-10}$ | $7.731 \cdot 10^{-11}$ | $5.2 \cdot 10^{-11}$ |
4. Conclusions

Let's formulate the main conclusions. First of all, we should note that the DLS method makes it possible to obtain regular data on the diffusion of SWCNTs and to study their properties. Then, using the Einstein–Stokes formula or relations more suitable for CNTs (see, for example, [16]), it is possible to obtain the size distribution of CNTs. The preparation of nanofluids with SWCNTs based on water always requires the use of a surfactant. In some cases, surfactant molecules form micelles and polymicelles, which also affect diffusion. Data on the diffusion coefficient in a wide range of mass concentrations of nanotubes (from 10^{-5} to 0.01%) were obtained for the first time. With an increase of the SWCNT concentration, their diffusion coefficient changes almost linearly; however, this change is relatively small.

The MD simulation allows neglecting the effect of surfactants and focusing on the features of the interaction of the nanotubes themselves with the base liquid. Even fairly simple CNT models used make it possible to obtain not only qualitative, but also quantitative results. In addition, the MD method allows one to study characteristics that are difficult to measure in an experiment. As an example, we can mention the research of diffusion anisotropy by determining the diffusion coefficients in the longitudinal and transverse directions to the nanotube axis. Another important characteristic is the rotational diffusion coefficient.

The obtained values of the diffusion coefficient of CNTs are compared with the known formulas describing the diffusion of long rods. It is shown that they agree with high accuracy with the formula usually used in the interpretation of experimental data [16]. Finally, the simulation data are compared with the experimental data.

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References

[1] Saeed Ė and Ibrahim Ė 2013 Carbon Letters 14(3) 131–44
[2] Saxena H G and Raj J 2017 Int. J. Eng. and Management Research 7(1) 304–11
[3] Krestinin A V 2019 Nanotechnologies in Russia 14(9–10) 411–26
[4] Zhao X and Liu R 2012 Environment International 40 244–55
[5] Espinosa C, Ortiz-Trujillo I C, Carlos-Cornelio J A, Zapata-Hernández R D and Hoyos-Palacio L M 2017 DYNa 84(203) 24–30
[6] Estellé P, Halelfad S and Maré T J 2017 Therm. Anal. Calorim. 127(3) 2075–81
[7] Rudyak V Ya, Minakov A V and Pryazhnikov M I 2021 J. Molecular Liquids 329 115517
[8] Rao R, Lee J, Lu Q, Keskar G, Freedman K O, Floyd W C, Rao A M and Ke P C 2004 Appl. Phys. Lett. 85 4228
[9] Judkins J, Lee H H, Tung S and Kim J W 2013 J. Biomed. Nanotechnol. 9(6) 1065–70
[10] Rudyak V, Krasnolutskii S, Belkin A and Lezhnev E 2020 J. Therm. Anal. Calorim. 10.1007/s10973-020-09873-8
[11] Girifalco L A and Lad R A 1956 J. Chem. Phys. 25(4) 693–7
[12] Nose S 1984 Mol. Phys. 52 255–68
[13] Hoover W G 1985 Phys. Rev. A 31 1695
[14] Rudyak V Ya, Aniskin V M, Maslov A A, Minakov A V and Mironov S G 2018 Micro- and Nanoflows (Fluid Mechanics and Its Applications vol 118) (Cham: Springer) p 240
[15] Rudyak V Ya, Belkin A A, Ivanov DA and Egorov V V 2008 High. Temp. 46 30–9
[16] Dhont J K G and Briels W J 2004 Rod-like Brownian particles in shear flow (Berlin: WILEY-VCH Verlag Berlin GmbH) p 116