Measuring the diffusion coefficient of single-wall carbon nanotubes in liquids

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Abstract. This work is devoted to the experimental study of the diffusion of single-walled carbon nanotubes in liquids. The mass concentration of nanotubes varied from 0.00001 to 0.15. As the base fluid, water is used with the addition of two different surfactants: polyvinylpyrrolidone and sodium dodecylbenzenesulfonate. The concentration of surfactant is two times the concentration of nanotubes. The measurements are performed using the dynamic light scattering method. The diffusion and sizes of surfactant molecules have been preliminary studied. The diffusion coefficient of carbon nanotubes are investigated. Using these data the size distributions of nanotubes are obtained. The dependence of diffusion coefficients on the concentration of carbon nanotubes is examined.

1. Introduction
Carbon nanotubes (CNTs) were discovered almost three decades ago [1]. CNTs are a rather complex phenomenon. Depending on the technology of their production, CNTs may be single-walled, double-walled or multi-walled. The diameter of single-walled CNTs is 1–2 nm, while the length can reach hundreds of nanometers or even more. In multi-walled CNTs, the diameter can reach several tens of nanometers, and the distance between the layers is actually of the order of the characteristic size of the molecules.

CNTs have a number of unique thermal, electrical, and mechanical properties. They can be conductive or have semiconductor properties. The thermal conductivity of multi-walled CNTs exceeds 3,000 W / m, while in single-wall SWCNTs it is two times as high. Nanotubes possess unique mechanical properties, combining both high strength and high elasticity [2]. The uniqueness of the properties of CNTs makes them very popular in a variety of applications: in electronics, when creating materials with unique properties, a new type of filters, supercapacitors, batteries, various types of sensors, etc. (see, for example, [3] and the references therein). Many of these applications are already implemented. In practice, however, in almost all cases, the use of CNTs requires the preliminary creation of the corresponding nanofluids. These nanofluids, however, differ significantly from ordinary nanofluids with spherical particles. This is due to two circumstances: first, a large ratio of the CNT length to its diameter, reaching hundreds and thousands. On the other hand, CNTs form conglomerates of tubes due to strong van der Waals interactions. The formation of conglomerates is also characteristic of spherical particles, but CNTs in the base fluid create complex network structures. Therefore the structure of nanofluids with CNTs changes significantly.
Thus, the study of transport processes in nanofluids with CNTs is extremely important. Over the past twenty years, dozens of papers have been devoted to the study of the thermophysical properties of nanofluids with CNTs. Thermal conductivity and viscosity were mainly studied (see, for example, [4–11] and the literature cited there). Nevertheless, the formulation of some final conclusions is extremely difficult. This is due to the fact that almost all the known data correspond to virtually different nanofluids, since they were obtained for, generally speaking, different CNTs using various surfactants and ultrasonic processing powers. Until now, there have been almost no research works experimentally studying the diffusion of CNTs. Only two or three such works are known. Thus, in papers [12, 13], the diffusion of CNTs was studied by means of single-molecular fluorescence microscopy. This was done with some medical purposes. The values of diffusion coefficients obtained in these works, however, differed quite strongly. The lack of experimental information stimulated the appearance of several studies where the diffusion of CNTs was modeled by the molecular dynamics method [14, 15]. The data presented here are certainly useful, although it should be noted that the fairly model systems were considered. This brief review shows that the experimental study of the diffusion of CNTs is relevant. The aim of this work is to experimentally study the diffusion of single-walled CNTs in liquids and to determine the size of CNTs by the light scattering method.

2. Method of measure and materials

Nanofluids for the purposes of this work were prepared by the standard two-step method [16]. In this work, water (W) was used as the initial base fluid. In the first step, the required amount of CNTs powder was added to the original base liquid, after which the resulting suspension was thoroughly mechanically mixed. Then, the obtained primary nanofluid was subjected to ultrasonic treatment. Creating base fluids is a serious problem in itself. CNTs have a very large surface area and, as a result, high values of surface energy. For this reason, when creating base fluids for nanofluids with CNTs, it is almost always necessary to use surfactants.

Practice usually requires applying two different approaches: steric and electrostatic. In the first case, surfactants on the surface of nanoparticles create a steric barrier that prevents their agglomeration. During electrostatic stabilization, a surfactant creates a double electric layer, providing repulsion of nanoparticles. The choice of surfactant is also largely determined by the initial base fluid. In this work, two different types of surfactants were used: anionic, i.e., sodium dodecylbenzenesulfate (SDBS), \( \text{CH}_3(\text{CH}_2)_7\text{CH}_3\text{SO}_3\text{Na} \), and non-ionic, i.e., polyvinylpyrrolidone, \( (\text{C}_6\text{H}_9\text{NO})_n \) (PVP).

The diffusion of single-walled CNTs manufactured by OCSiAl, Novosibirsk, was studied. The weight concentration of SWCNTs varied from 10\(^{-1}\) to 10\(^{-5}\)% . The weight concentration of surfactants was two times the concentration of SWCNTs. The measurements were carried out at a temperature of 25°C. Both base fluids are Newtonian and low viscosity. Their viscosity and rheology were studied using Brookfield DV3 RV and DV3T LV rotational viscometers. The accuracy of measuring the viscosity coefficient was about 2%. At a maximum weight concentration of the surfactant equal to 1%, the viscosity of both solutions (W + SDBS and W + PVP) exceeded the viscosity of water by about 2–3%.

The diffusion of CNTs in base fluids was studied using dynamic light scattering method. In this work the Malvern Zetasizer ZSP device was applied. The range of particle sizes measurable by this device is from 0.3 nm to 10.0 microns. For measurement, 1 ml of nanofluid was diluted to the required concentration of CNTs; then, the sample was thermostated at a temperature of 25°C. Each measurement was performed several times, and then, the results were averaged.

During the experiment, the intensity of light scattered by the particles was measured and the corresponding two-time correlation function was constructed. Using this correlation function, the diffusion coefficient \( D \) of the particles under investigation was then determined. As a result, a certain distribution of diffusion coefficients as a function of the scattered light intensity was found. Each value in this distribution, generally speaking, corresponded to reflection from particles of a given size. Therefore, according to these distributions, one can obtain data on the size distribution of particles in the nanofluid. For this, the Stokes–Einstein formula is usually used.
\[ D = \frac{kT}{6\pi\eta R}. \]  

(1)

Here \( \eta \) is the viscosity coefficient of the carrier fluid, \( T \) is the temperature, \( R \) is the radius of the dispersed particle, and \( k \) is the Boltzmann constant.

Strictly speaking, formula (1) is applicable only for spherical particles of radius \( R \). Therefore, when applied to nonspherical particles, it is customary to call it the hydrodynamic radius. For nonspherical particles, relation (1) is modified, in particular, for cylindrical tubes of length \( L \) and diameter \( d \), it takes the following form [17]

\[ D_c = \frac{kT}{6\pi\eta L} \left( \ln \frac{L}{d} + 0.32 \right). \]  

(2)

The method testing was performed on spherical latex particles with a given average size: 246, 522, and 1028 nm. The measurement accuracy turned out to be sufficiently high, and the particle size distributions were lognormal.

3. Results of the measurements

The base fluids used are quite complex, they include surfactants with large molecules. The presence of such molecules should have been recorded during the measurement. In order to be able to unambiguously identify SWCNTs, it was necessary to preliminarily study the diffusion of the surfactants molecules and determine their effective sizes. Fig. 1 presents the data of such measurements. Here Figs. 1a and 1b show the distributions of the sizes of PVP and SDBS molecules, respectively. When determining the effective size according to the diffusion coefficient, formula (1) was used. Thus, the Fig 1 presents the effective hydrodynamical diameter of these molecules. The average size of PVP molecules is equal to 282 nm. The maximum of the first peak of the light intensity \( I \) for SDBS molecules (Fig. 1b) corresponds to a particle size of 4.19 nm. According to molecular dynamics modeling [18], SDBS micelles have a diameter of 4 nm, which is quite consistent with the data obtained. The presence of the second peak corresponds to larger micelles of a different shape, which were reported in [19]. In this regard, it is interesting to note that this surfactant (SDBS) is not just a micellar solution, but it is also characterized by their polymorphism. In the first case, spherical aggregates are formed from SDBS molecules, and in the second, a certain analog of a nanotube. Namely these last structures generate the second peak in Fig. 1b. The average size of this second structures is about 110 nm.

![Figure 1. The size distributions of PVP a) and SDBS molecules b).](image)

The used dynamic light scattering method well identifies the diffusion of SWCNTs in the considered base liquids. The SWCNT size distributions in both base fluids are shown in Fig. 2. The data for two nanofluids with a mass concentration of SWCNTs equal to 0.02% are presented here; the concentration of both surfactants was twice as high. The solid and dashed lines correspond to SWCNT size distributions for nanofluids based on W+PVP and W+SDBS, respectively. The dash and dash-
dotted lines give the distributions of SDBS and PVP molecules. As before, the restoration of particle size was carried out using relation (1).

It is important to note that the characteristic sizes of SWCNTs are almost the same when using both surfactants. On the other hand, the distributions of PVP and SDBS molecules are localized in their places (see Fig. 1). The maxima of the distributions of PVP and SDBS do not coincide with the corresponding maxima for SWCNTs.

![Figure 2](image1.png)

**Figure 2.** The size distributions of SWCNTs in two different nanofluids. Solid and dashed lines correspond to the W+PVP and W+SDBS based nanofluids, respectively. Dotted and dash-dotted lines correspond to SDBS and PVP molecules, respectively.

The diffusion coefficient is determined for quite dilute suspensions. Strictly speaking, we are talking about the diffusion coefficient of an isolated dispersed particle, in particular, SWCNTs. In real experiments, there is always some quite finite concentration of particles in the carrier fluid. Simple estimates show that a sufficiently accurate value of the diffusion coefficient of SWCNTs is obtained if their weight concentration does not exceed $10^{-5}\%$. Naturally, with an increase in the concentration of SWCNTs, their diffusion coefficient will decrease.

![Figure 3](image2.png)

**Figure 3.** The dependence of the diffusion coefficients on the weight concentrations of SWCNTs. The solid line corresponds to the weight concentration of SWCNTs equal to 0.00001\%, the dashed line – to 0.01\%.
Fig. 3 shows the distribution of the diffusion coefficient depending on the weight concentration of SWCNTs. As a carrier liquid the water with SDBS surfactant was used. Here, the solid curve corresponds to the weight concentration of SWCNTs equal to 0.00001%, the dashed line is 0.01%. The largest value of the diffusion coefficient does occur at a minimum concentration of SWCNTs (solid line). The distribution has two maxima, which indicates that even at such low concentrations, the size distribution of SWCNTs is heterogeneous. The presence of a second maximum (right) refers to insulated small tubes. It is worth noting that the second maximum is observed at all concentrations of SWCNTs. However, the size of these small tubes changes approximately five times.

The maximum value of the SWCNTs diffusion coefficient $D$, corresponding to the first maximum of the light intensity, is $D = 2.3 \times 10^{-12}$ m$^2$/s. At the following concentrations, the maximum values of the diffusion coefficient have corresponding values: $D = 1.2 \times 10^{-12}$ m$^2$/s and $D = 0.4 \times 10^{-12}$ m$^2$/s. These, as already mentioned, are the maximum values. The average ones are slightly lower. The latter value for a concentration of 0.01% is in good agreement (within 10%) with the data of [12], but there the SWCNTs were coated with either a ribonucleic acid polymer (RNA) or bovine serum albumin (BSA). In paper [13], the diffusion coefficient values exceeding our data for a concentration of 0.01% by about an order of magnitude were obtained, but the completely different basic fluids (many times more viscous) were used in this work.

Until now, when interpreting data on the diffusion of SWCNTs by their size (see Figs. 1 and 2), the Stokes–Einstein formula (1) was used, that is, their effective hydrodynamical radius (or corresponding diameter) was determined. However, for practical purposes, and when conducting laboratory experiments, it is usually necessary to know the characteristic diameter and length of SWCNTs or their bundles in the studied or used nanofluids. The conducted experiments allow us to obtain such information. The length distribution of SWCNTs in water-based nanofluids with two different surfactants is shown in Fig. 4. Here, the solid line corresponds to nanofluid with SDBS, and the dashed line corresponds to PVP. The weight concentration of SWCNTs in both cases was the same and equal to 0.15%, and the surfactant was 0.3%. When restoring the length of SWCNTs from the measured values of the diffusion coefficient, formula (2) was used, where the average radius of the SWCNT bundles was taken to be 10 nm.

![Figure 4](image_url)

**Figure 4.** The length dependences of SWCNTs in W+PVP (dotted line) and W+SDBS (solid line) based nanofluids.

In accordance with the distributions presented in Fig. 4, two characteristic circumstances should be noted. First, the average sizes of SWCNTs when using various surfactants differ significantly. So, if SDBS is used to prepare the base fluid, the average tube bundle size is about 2.6 μm. Whereas in nanofluids with PVP, the average tube size exceeds 3 μm. The second important circumstance is that
in all cases the size distributions have two maxima. The first corresponds to low intensity and identifies individual tubes, which are almost always present in nanofluids, unless their concentrations are too high. The characteristic size of these tubes is the same in both nanofluids. Their thickness is 1.6 nm, and the average length is almost an order of magnitude less than that of beams.

![SWCNTs distributions over the hydrodynamic diameter in W+SDBS based nanofluids before (red line) and after (green line) centrifugation](image)

Figure 5. SWCNTs distributions over the hydrodynamic diameter in W+SDBS based nanofluids before (red line) and after (green line) centrifugation

In practice, centrifugation of nanofluids is often used to obtain SWCNTs of a given size. This is indeed a fairly effective method for differentiating CNTs by size. An example of the results of such centrifugation in W+SDBS based nanofluids is shown in Fig. 5. The weight concentration is equal to 0.1%. Centrifugation was carried out during 30 minutes on a unit with an angular speed of 14,000 rpm. Even after such a short centrifugation, the length of the SWCNTs decreased by about 17% from 406.9 to 337.7 nm.

Conclusion
In conclusion, it can be noted that the dynamic light scattering (DSL) method is a rather effective method for measuring the diffusion coefficient of SWCNTs. Using the data obtained in this way, one can then obtain the information on the sizes of SWCNT bundles. It should be understood, of course, that SWCNTs have a significant ratio of the length of the tubes (or their bundles) to their diameter. The aspect ratio can reach hundreds and even thousands. Therefore, the use of Eq. (1) for interpretation allows us to determine only the so-called effective hydrodynamical radius (diameter) of SWCNTs. This radius is several times smaller than the actual length of the tubes. The length of SWCNTs can be determined fairly accurately using formula (2). Its application, however, requires accurate knowledge of the diameter of nanotubes or their bundles. The exact diameter of the isolated SWCNTs is known, it is 1.6 nm. This value can be used in interpreting data on the diffusion of highly diluted nanofluids. However, in the general case, there are bundles of nanotubes in a nanofluid, the average diameter of which substantially exceeds the diameter of an insulated tube. Therefore, in order to correctly restore the length of nanotubes from the data of the diffusion coefficient measurements, it is necessary to simultaneously study them using electron microscopy.

There is one more important circumstance. SWCNTs are essentially nonspherical nanoparticles. Therefore, along with the usual translational diffusion, their rotational diffusion should be studied also. The study of this type of diffusion is also of considerable practical interest (especially in different bi-
medical application, in MEMS and NEMS and etc.). However, its identification according to DLS method is virtually impossible, or at least requires special methods of interpretation of the obtained experimental data. For these purposes such methods as depolarized dynamic light scattering, polarized fluorescence recovery after photobleaching and nuclear magnetic resonance may be used [20–22].

Measurements of the diffusion coefficient of the two nanofluids under consideration (W+PVP and W+SDBS based) have shown that the latter surfactant is more effective (see Fig. 4). At the same time, it should be noted that PVP is a rather complex surfactant, containing \( n \) C\(_6\)H\(_{2n+1}\)O fragments. The effectiveness of this surfactant strongly depends on the value of \( n \). In presented experiments, PVP was used with \( n \) equal to several tens (see Fig. 1a). By varying \( n \), one can increase or decrease the effectiveness of given surfactant.

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