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Acoustic spectroscopy for evaluating dimensions of cylindrical carbon nano-objects in colloidal systems

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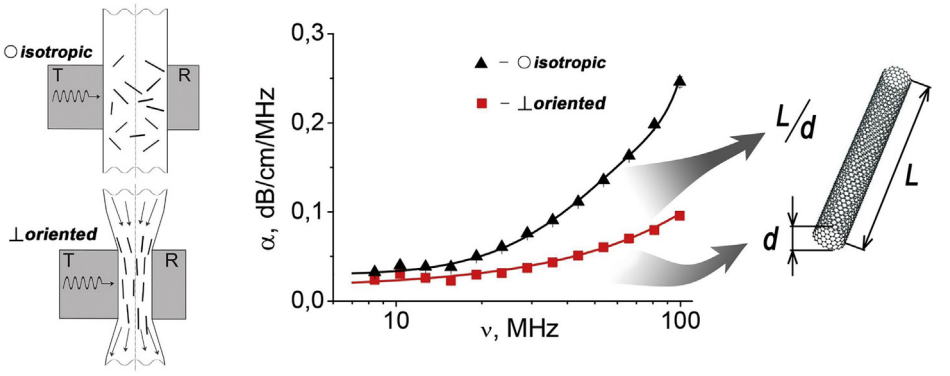
HIGHLIGHTS

- A method for evaluating dimensions of cylindrical objects in colloids is proposed.
- The mechanism relies on orienting nano-objects along accelerated flow of colloid.
- Alignment of nano-objects is controlled by measuring viscosity of colloid.
- A diameter is calculated for cylindrical objects oriented across ultrasonic wave.
- An aspect ratio is evaluated from spectra of oriented and non-oriented objects.

GRAPHICAL ABSTRACT



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ABSTRACT

Ultrasound attenuation spectroscopy was applied to develop an express method for determining two dimensions of cylindrical nano-objects in colloids. For this we offered to perform measurements of attenuation spectra for two independent states of colloids: with the isotropic distribution of nano-objects and with orientation of nano-objects across the ultrasound beam. The oriented state of the nano-objects is achieved in the flowing colloid due to flow acceleration in the constricted channel. As a criterion of maximum orientation of nano-objects along the flow we used the decreasing of longitudinal viscosity close to the asymptotic value. A significant difference was found between attenuation spectra measured in two states for three aqueous colloids of carbon nanotubes and nanofibers with aspect ratio from 27 to 415. The diameter values from 5 to 21 nm of the nano-objects, calculated from attenuation spectra of oriented state, corresponded to TEM and AFM data. We suggested the methodology for evaluation of the aspect ratio of the cylindrical nano-objects in colloids based on the attenuation spectra in two states of colloids and the calibration function which should be preliminary defined using acoustic and microscopy tests of reference colloids.

1. Introduction

For the last two decades, the ultrasound attenuation spectroscopy of compressional longitudinal waves in liquid has become a widely used method for the determination of particle size dis-

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tributions and rheological behavior of complex colloidal systems, without diluting them [1]. Acoustic attenuation spectra are interpreted in terms of analytical models, taking into consideration the spherical form of particles [2–6]. To model the relationship between particle size distribution and ultrasound attenuation measurements the ECAH theory developed by Epstein and Carhart [2] and Allegra and Hawley [3] is the one most commonly used. This theory is based on a mathematical description associated with the propagation of an ultrasonic wave through a liquid containing an ensemble of spherical particles. The ECAH model has shown that ultrasonic attenuation can be accurately characterized through fundamental equations based on the laws of conservation of mass, energy, and momentum, the thermodynamic equations of state, and stress–strain relations for isotropic elastic solids and viscous fluids. Later in 1996 Dukhin and Goetz extended the ECAH theory for concentrated dispersions and colloids taking in consideration particle-particle hydrodynamic interactions [4,6]. For providing high precision of measurements of micro- and nano-particulates dimensions, the reference colloids with the spherical particles of the given size are used, e.g. colloidal silica [7].

However, a large number of industrial colloidal systems (dispersions) contain objects of the form considerably different from the spherical one, i.e. ceramic nanorods, organic fibers, aluminosilicate platelets, among others. In technological processes, the express measurements of non-spherical nano-objects as a part of colloids are very important with the purpose of control of dispersing and stabilizing the colloids and orienting nano-objects. The majority of non-spherical nano-objects comprise cylindrical carbon nanoparticles: nanotubes and nanofibers, industrial application of which is growing rapidly. Such nano-objects are characterized by the high ratio of the length of the object to its diameter, i.e. aspect ratio, about 10^2–10^3, which prevents wide application of the approaching of the nano-object by an equivalent sphere [8]. Therefore, the usage of ultrasound attenuation spectroscopy was limited for defining of dimensions of non-spherical objects.

A number of important theoretical and experimental studies describe the interaction of ultrasound with non-spherical objects in liquids [9–15]. Regarding the sound attenuation due to the visco-inertial coupling between particles and fluid, the theoretical consideration implies that shape effects have to be included via the oscillatory drag force of non-spherical particles. Using this approach Ahuja and Hendee described the attenuation of prolate and oblate spheroids, with their symmetry axis aligned either perpendicular or parallel to the incident sound field [9]. The set of theoretical publications confirmed that ultrasound attenuation depends on the aspect ratio and orientation of non-spherical objects and, therefore, can be used for their characterization. In particular, it was shown by Babick and Richter [8] on the models of oblate and prolate spheroids that the difference between attenuation spectra of variously oriented objects in liquid is rising with the increase of their aspect ratio.

In the set of experimental studies [13–15] the ultrasound attenuation technique was found to be capable of monitoring the size and concentration of anisotropic particles and it was responsive to the length and width of the needle-shaped crystals, e.g., L-glutamic acid and urea. The particle size distribution derived from ultrasonic attenuation spectra was described as consistently bimodal, the mean sizes of the two modes being close to the width and length of the crystals on the basis of microscope images. It was seen that the particle size distributions obtained gave some insight into characterizing the shape of the nonspherical particles.

Experimentally, the effect of the influence of orientation of the cylindrical non-spherical nano-objects in liquid on ultrasound attenuation spectra was discovered in the use of the modern acoustic spectrometer DT-1202 (Dispersion Technology, USA), which allowed to orient nano-objects in the cylindrical measurement cell with the help of accelerated or decelerated hydrodynamic flow of colloid [16]. Attenuation spectra in the aqueous colloid of carbon nanotubes, measured by the instrument with the preferentially parallel and perpendicular orientation to the ultrasound wave direction, are considerably different in the form and magnitude. Obviously, the difference between the two spectra can tell us about the geometrical dimensions of non-spherical nano-objects in colloid, though their quantitative definition is quite hard because of the absence of the nano-objects' orientation control. Such experiments make it possible to give qualitative information on the presence of non-spherical nano-objects and to provide hypothetical comparison of colloids with a different number of such objects.

The approach described in the present work is aimed at the development of the methodology of measuring sizes of non-spherical nano-objects in liquids, which shape can be close to cylindrical, characterized by the diameter and length. We are considering the case where the length is more than the diameter, though the similar approach can be applied for the opposite situation, when the length (disk thickness) is less than diameter. To define the two dimensions of cylindrical objects by the acoustic spectroscopy, it is important to measure the ultrasound attenuation for two independent states of colloid, different in the orientation of nano-objects, and use the respective analytical models for spectra interpretation. In the process, the creation of two states should be confirmed by the instrumental control and/or physical principles. As one of such states, it is recommended to use a colloid with the isotropic orientation of the bulk of non-spherical nano-objects, which is thermodynamically stable in the absence of hydrodynamic flow. As for the second state, it is convenient to examine colloid in a stationary flow with the bulk of the cylindrical nano-objects oriented along the flow, as such orientation can be realized by the flow speed management. With the use of the modern acoustic spectrometer for this state of colloid, the measurements can be made of the attenuation of ultrasound perpendicular to the flow direction and, therefore, perpendicular to the orientation of cylindrical nano-objects. The present research demonstrates the implementation of the above-mentioned approach applied to three aqueous colloids on the base of practically important carbon cylindrical nano-objects: nanotubes and nanofibers.

2. Materials and sample preparation procedures

We used three types of aqueous colloids on the base of weakly agglomerated carbon cylindrical nano-objects, the first of which, C-Tuball, was prepared from the purified nanocarbon product Tuball (OCSiAl Russia, Novosibirsk), containing 75% of single-walled carbon nanotubes (SWCNT), the second C-NCM from concentrated suspension of nanofibers NCM-A (Nanocarbon Materials, LLC, Gusev, Russia), and the third one C-Palizh from the suspension of carbon nanofibers Palizh (Noviy Dom, LLC, Izhevsk, Russia). The purification process of nanocarbon product Tuball by the well-known method [17] provided the removal of residual catalyst and never led to strong agglomeration of nano-objects. In the process of preparation of colloids C-Tuball и C-NCM, the original products were diluted by the deionized water in the presence of the dispersant sodium dodecylbenzenesulfonate (SDBS) for the steric stabilization of nano-objects. To remove large agglomerates of nano-objects from colloids, each colloid sample went through an intensive procedure of ultrasonication in a volume of about 150 ml, cooled with running water at 10 °C with the acoustic power of 100 W during 60 min and a procedure of accelerated sedimentation in the centrifugal field of 5000–9000 × g during 10–60 min using the high-speed centrifuge Sigma 3–30 K (Sigma Laborzentrifugen GmbH, Germany).