

L. A. Bulavin^{1,2}, O. V. Tomchuk^{1,3}, M. V. Avdeev³¹ Taras Shevchenko National University, Kyiv² Institute for Safety Problems of Nuclear Power Plants, National Academy of Sciences of Ukraine, Kyiv³ Joint Institute for Nuclear Research, Dubna, Russia**INVESTIGATION OF THE CLUSTER STRUCTURE IN AQUEOUS SUSPENSIONS OF NANODIAMONDS BY SMALL-ANGLE NEUTRON SCATTERING**

The paper presents the results of the structural study of various types of the water-detonation nanodiamond liquid systems, which are obtained by small-angle scattering of thermal neutrons. It was shown that in the mass fraction range (0.3÷1.8) % the experimental spectra are well described by a two-level model of unified exponential/power-law approach. The resulting structural parameters allowed us to estimate the aggregation number in the studied systems. Sizes of the nanodiamond particles and their clusters are found as well as the fractal dimension of the latter.

Keywords: detonation nanodiamonds, small-angle neutron scattering, fractal clusters, aggregation number.

Introduction

The general interest to carbon materials associated with wide opportunities of surface modification and functionalization for various applications [1]. Detonation nanodiamonds are produced by the explosion of oxygen-unbalanced explosives without any additional carbon source [2, 3]. The resulting nanocrystals is a promising material for nanotechnology [4], including biomedical applications [5]. This is a typical nanomaterial with an average particle size of about 5 nm [1, 2], which has preferably spherical shape. However, it is difficult to separate the nanodiamonds from by-products of the explosion. This is due to the formation of multi-level aggregation through non-diamond components. Recently a number of methods of the nanodiamond disaggregation were developed. In particular, it is dispersion in liquid carrier [6]. As a result, the large specific surface area leads to the formation of stable clusters within size range (10÷500) nm [6, 7]. Determining the structure and description of cluster growth in suspensions are the actual problems of modern nanotechnology. Also an important aspect of the studying such systems is the prospect of a non-aggregated nanodiamond suspension.

At present, nuclear physics methods studying nanosystems, including nuclear magnetic resonance, activation analysis and diffraction of various radiations *etc.*, are widespread. Important among these is small-angle scattering of X-rays and thermal neutrons, which registers the scattering from inhomogeneities far exceeding the wavelength of radiation [8]. The using of neutrons has several advantages in studies of light chemical elements, and allows contrast variation procedure by isotopic substitution in the solvent.

In previous papers we have carried out a structural diagnostics of liquid systems with nanodiamonds

based on polar solvents. It used small-angle neutron scattering method, which allows direct noninvasive studies of volume nanosystems. Thus, the optimal model describing scattering from cluster systems was determined [9] the internal structure of detonation nanodiamonds particles was studied [7, 9 - 12], the analysis of the aggregation mechanism in such systems was done [12, 13], and cluster-cluster interaction was studied [12]. With respect to structure, special attention was paid to the size of given structures and fractal dimension, reflecting internal interparticle correlations. The purpose of this paper is complete analysis structure of detonation nanodiamonds clusters in aqueous suspension including an experimental determination of the particles number in the nanodiamond clusters, which is the main objective of the present study.

Experiment

In this paper, we focus our attention on detonation nanodiamond aqueous suspensions of mass concentration up to 2 %. Such concentrations allow, firstly, to apply small-angle neutron scattering for studying the of the nanodiamond cluster suspensions structure, secondly, to avoid the influence of structure factor, *i.e.* interaction effects on the scattering [8], as, for example, has been received for a certain class of magnetic fluids [14]. On the one hand low content of dispersed phase in the system decreases the small-angle scattering signal, because the spectrum is proportional to the concentration. On the other hand, good contrast characteristics of the system (the scattering length density of diamond is $11.8 \cdot 10^{10} \text{ cm}^{-2}$ versus $-0.56 \cdot 10^{10} \text{ cm}^{-2}$ for light water) allows one spectrum detection with a good accuracy against the residual incoherent background because a differential cross section is proportional to the square of contrast (the difference between the scattering length densities of particles and solvent).

© L. A. Bulavin, O. V. Tomchuk, M. V. Avdeev, 2015

Various modifications of detonation nanodiamond aqueous suspensions, which are presented in the Table, were investigated. The first suspension DUNCD (system 1) was made in Nanocarbon Research Institute (Nagano, Japan) by stirred-media milling under powerful ultra-sonication [2, 6] of commercial powders from Gansu Lingyun Nano-Material Co. Ltd. (Lanzhou, China). Suspensions DND1 and DND2 (systems 2 - 3) were synthesized in Ioffe Physical-Technical Institute (St. Petersburg, RF) following the procedure described by Aleksenskii and Eydelman [15]; initial detonation nanodiamond powder from the Federal State Unitary Enterprise "Technolog" (St. Petersburg, RF).

Also for the samples production commercial powders of detonation nanodiamonds RUDDM (Real-Dzerzhinsk, Dzerzhinsk, RF) and SDND (PlasmaChem GmbH, Berlin, Germany) were used [12]. The initial aqueous suspensions were prepared by dispersing the powder in water. Then they subjected to vigorous stirring for 30 min and ultrasonic treatment for 1 h. Further suspensions were centrifuged at 25000 rev/min (relative centrifuge strength is 49000g at $r_{\max} = 7.01$ cm) during 45 or 90 min. In each case light and heavy fractions were formed. Liquid systems SDND90, RUDDM45 and RUDDM90 (systems 5 - 7) are appropriate light fractions. SDNDL suspension (system 4) was received by SDND90 drying and following re-dispersion into water.

Small-angle neutron scattering experiments were carried out on SANS-1 diffractometer, located at the FRG-1 steady-state reactor, Helmholtz-Zentrum Geesthacht (Geesthacht, Germany) [16], as well as on YuMO small-angle time-of-flight two-detector diffractometer at the IBR-2 pulsed reactor, Joint Institute for Nuclear Research (Dubna, RF) [17, 18]. As a result of experiments for different systems differential scattering cross section, isotropic over radial angle φ in the detector plane, per unit volume of sample (scattered intensity) was obtained as a function of the modulus of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the incident neutron wavelength and θ is the scattering angle.

Results and discussion

Small-angle neutron scattering spectra for different aqueous suspensions of detonation nanodiamonds are shown in Fig. 1. There are two regions of power-law dependence, $(0.2 \div 0.9)$ and $(1 \div 2)$ nm⁻¹, which are linear in double logarithmic scale. Therefore, scattering reflects a two-level organization of particles in suspensions, the cluster level and the level of nanodiamond particles themselves (Fig. 2 for details).

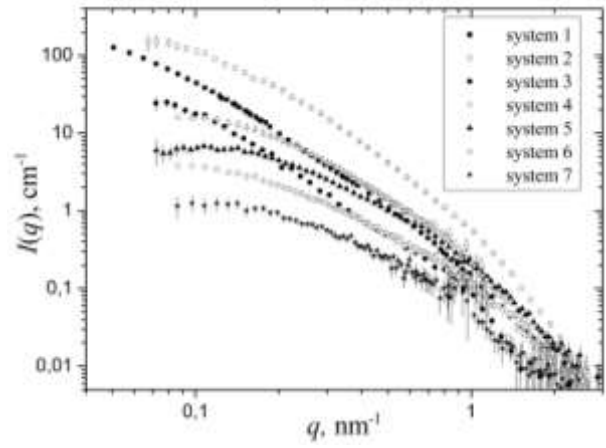


Fig. 1. Small-angle neutron scattering spectra for different water-detonation nanodiamond suspensions.

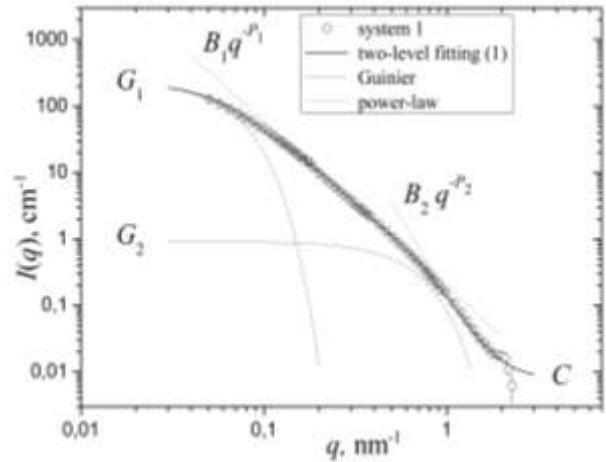


Fig. 2. An example of the small-angle neutron scattering spectrum for detonation nanodiamond suspension (points). Solid line shows the fitting according to the unified exponential/power-law approach. Dot lines indicate the power-law scattering regimes for cluster structure (small q -values) and diffusive surface of detonation nanodiamond particles (large q -values). Guinier regimes for two scattering levels are shown by dash lines.

Small-angle neutron scattering curves of the investigated systems can be fitted in a frame of a two-level model of the unified exponential/power-law approach [9,20]:

$$I(q) = G_1 \exp(-q^2 R_{g1}^2 / 3) + B_1 \exp(-q^2 R_{g2}^2 / 3) \times \\ \times (\operatorname{erf}(qR_{g1} / 6^{1/2}) / q)^{P_1} + G_2 \exp(-q^2 R_{g2}^2 / 3) + \\ + B_2 (\operatorname{erf}(qR_{g2} / 6^{1/2}) / q)^{P_2} + C, \quad (1)$$

where the parameters with '1' and '2' indices refers to the clusters scattering level and the composing nanodiamond particles scattering level, respectively; R_g is gyration radii, some characteristic sizes; P is the exponents of power-law scattering that characterize intraparticle correlations; G and B are related to the density of scattering centers and neutron con-

trast; C is residual incoherent background that is always present in the experiments, especially for the hydrogen-containing systems.

In fact, at each level scattering Eq. (1) combines Guinier regime that contains information about the size and the total amount of matter that scatters, and power-law regime that characterizes the internal structure. Thereby, Eq. (1) describes whole small-angle neutron scattering curve that allows to avoid the uncertainties in the approximation of separated spectrum regions using simple functions. The concentration range (0.3÷1.8) % allows one to detect both scattering levels, whereas the more dilute liquid system (~ 0.1 %) make it possible to detect only the scattering level of the clusters [13].

Power-law type of mentioned spectrum regions, which differs from the Porod law ($I(q) \sim q^{-4}$), indicates that the investigated system exhibits fractal properties [19], *i.e.* clusters are not tightly packed, and the surface of the detonation nanodiamonds particles is characterized by heterogeneous distribution of the scattering length density [11]. Thus, for all investigated systems P_2 is greater than 4, which means presence of certain scattering length density modulations on the surface of nanodiamonds, which correspond to the so-called diffuse surface type [10, 11]. Organization of nanodiamond clusters is fractal-like that follows from the value of the exponent $P_1 \sim 2.40 < 3$; this means that one have deal with branched aggregates [19]. In addition, the fractal dimension values, which are close for all suspension independently of the synthesis conditions, suggest a common aggregation mechanism in such systems. It was reported that it is close to the diffusion limited aggregation model [9, 12].

The characteristic nanodiamond particle radius R_{g2} for all systems lies in the relatively narrow range (1.7÷2.8) nm. A cluster gyration radius R_{g1} is presented in the Table and depending on the system varies from 6 to 27.2 nm.

**Structural parameters
of the nanodiamond suspensions**

System	Suspension	Mass fraction, %	R_{g1} , nm	N_{cl}
1	DUNDC	1	27.2 ± 5	256 ± 8
2	DND1	1.8	16.2 ± 0.31	143 ± 10
3	DND2	0.31	15.6 ± 1.1	160 ± 70
4	SDND L	0.5	7.63 ± 0.23	75 ± 10
5	SDND90	1.5	7.1 ± 0.17	79 ± 13
6	RUDDM45	0.8	8.31 ± 0.05	84 ± 4
7	RUDDM90	0.4	6.0 ± 0.4	3 ± 2

Forward scattering intensity of both levels, G_1 and G_2 , are appropriate asymptote of the Guinier-type terms (first and third terms in Eq. (1)) for small

scattering vector modulus values for each curve of small-angle scattering. For clusters of monodisperse particles:

$$G_1 \sim \langle N^2 \rangle, \quad (2a)$$

$$G_2 \sim \langle N \rangle, \quad (2b)$$

where N is number of particles in a particular cluster, $\langle \dots \rangle$ means averaging over all clusters in a system. So the estimation of the aggregation number, *i.e.* the average number of particles in the cluster, can be obtained as [21]:

$$N_{cl} = G_1/G_2 = \langle N^2 \rangle / \langle N \rangle. \quad (3)$$

The results are presented in the Table. One can see that the cluster size as well as the number of particles is sensitive to the synthesis conditions and the initial concentration of nanodiamonds in the system. Small-angle neutron scattering method allows to determine the aggregation number N_{cl} . However, for low concentrated systems of small clusters the experimental error increases. This is due to the influence of residual incoherent scattering background in experimental spectra. The source of mentioned background mainly is protons from the water. Full background removal by replacing the protonated solvent to deuterated not fundamentally improve the results, because in this case the neutron contrast will be significantly reduced, because the scattering length densities of heavy water is $6.34 \cdot 10^{10} \text{ cm}^{-2}$. The difference between the scattering length densities of particles and liquid carrier reduced to ~ 2.3 times, and in turn small-angle neutron scattering signal reduced to ~ 5.1 times. Still correlation between the gyration radius and the aggregation number is well evident: they are growing simultaneously, indicating the accuracy of the analysis.

Conclusions

The small-angle neutron scattering experiments allows one to determine the structure of detonation nanodiamonds cluster suspensions based on water. The obtained experimental structural parameters of nanodiamond particles that describe the size and nature of the surface are consistent for all studied systems. The investigated clusters are characterized by fractal structure (fractal dimension ~ 2.4). It is proved that the small-angle neutron scattering can be used for direct determination of an aggregation number of the nanodiamond particles in suspensions. It is shown that some synthesis methods allow obtaining the liquid systems containing clusters of about ten nanodiamond particles and the size of the order of 10 nm.

REFERENCES

1. *Shenderova O.A., Zhirnov V.V., Brenner D.W.* Carbon nanostructures // *Crit. Rev. Solid State Mater. Sci.* - 2002. - Vol. 27. - P. 227 - 356.
2. *Osawa E.* Monodisperse single nanodiamond particulates // *Pure Appl. Chem.* - 2008. - Vol. 80. - P. 1365 - 1379.
3. *Dolmatov V.Yu.* Ultradisperse diamonds of detonation synthesis: properties and applications // *Uspekhi Khimii.* - 2001. - Vol. 70, No.7. - P. 687-708. (Rus)
4. *Krüger A., Ozawa M., Jarre G. et al.* Deagglomeration and functionalisation of detonation diamond // *Phys. Status Solidi A.* - 2007. - Vol. 204. - P. 2881 - 2887.
5. *Chao J.I., Perevedentseva E., Chung P.H. et al.* Nanometer-sized diamond particle as a probe for biolabeling // *Biophys. J.* - 2007. - Vol. 93. - P. 2199 - 2208.
6. *Krüger A., Kataoka F., Ozawa M. et al.* Unusually tight aggregation in detonation diamond: identification and disintegration // *Carbon.* - 2005. - Vol. 43. - P. 1722 - 1730.
7. *Avdeev M.V., Rozhkova N.N., Aksenov V.L. et al.* Aggregate Structure in Concentrated Liquid Dispersions of Ultrananocrystalline Diamond by Small-Angle Neutron Scattering // *J. Phys. Chem. C.* - 2009. - Vol. 133. - P. 9473 - 9479.
8. *Feigin L.A., Svergun D.I.* Structure analysis by small-angle x-ray and neutron scattering. - New York: Plenum Press. - 1987. - 335 p.
9. *Tomchuk O.V., Avdeev M.V., Bulavin L.A. et al.* Small-angle neutron scattering by fractal clusters in aqueous dispersions of nanodiamonds // *Physics of Particles and Nuclei Lett.* - 2011. - Vol. 8, No. 10. - P. 1046 - 1048.
10. *Avdeev M.V., Aksenov V.L., Tomchuk O.V. et al.* The spatial diamond-graphite transition in detonation nanodiamond as revealed by small-angle neutron scattering // *J. Phys.: Condens. Matter.* - 2013. - Vol. 25. - P. 445001 (7 p).
11. *Tomchuk O.V., Bulavin L.A., Aksenov V.L. et al.* Small-angle scattering from polydisperse particles with a diffusive surface // *J. Appl. Cryst.* - 2014. - Vol. 47. - P. 642 - 653.
12. *Tomchuk O.V., Volkov D.S., Bulavin L.A. et al.* Structural characteristics of aqueous dispersions of detonation nanodiamond and their aggregate fractions as revealed by small-angle neutron scattering // *J. Phys. Chem. C.* - 2015. - Vol. 119. - P. 794 - 802.
13. *Tomchuk O.V., Avdeev M.V., Aksenov V.L. et al.* Comparative structural characterization of the water dispersions of detonation nanodiamonds by small-angle neutron scattering // *J. Surf. Inv. X-ray, Synchr. Neutr. Techn.* - 2012. - Vol. 6, No. 5. - P. 821 - 824.
14. *Nagornyy A.V., Bulavin L.A., Petrenko V.I. et al.* Determination of the structure factor of interparticle interactions in the ferrofluid by small-angle neutron scattering // *Nucl. Phys. Atom. Energ.* - 2013. - Vol. 58(8). - P. 735 - 741. (Ukr)
15. *Aleksenskii A.E., Eydelman E.D., Vul' A.Y.* Deagglomeration of detonation nanodiamonds // *Nanosci. Nanotechnol. Lett.* - 2011. - Vol. 3. - P. 68 - 74.
16. *Zhao J., Meerwinck W., Niinkoski T. et al.* The polarized target station at GKSS // *Nucl. Instrum. Methods Phys. Res. A.* - 1995. - Vol. 356. - P. 133.
17. *Ostanevich Y.M.* Time-of-flight small-angle scattering spectrometers on pulsed neutron sources // *Macromol. Chem., Macromol. Symp.* - 1988. - Vol. 15. - P. 91 - 103.
18. *Kuklin A.I., Islamov A.Kh., Kovalev Yu.S. et al.* Optimization of the two-detector system of the YuMO small-angle neutron spectrometer for investigation of nanoobjects // *Poverkhnost'. Rentgenovskie, Sinkhrotronnye i Neitronnye Issledovaniya.* - 2006. - No. 6. - P. 73 - 84. (Rus)
19. *Schmidt P.W.* Small-angle scattering studies of disordered, porous and fractal systems // *J. Appl. Cryst.* - 1991. - Vol. 24. - P. 414 - 435.
20. *Beaucage G.* Small-angle scattering from polymeric mass fractals of arbitrary mass-fractal dimension // *J. Appl. Cryst.* - 1996. - Vol. 29. - P. 134 - 149.
21. *Beaucage G., Kammler H.K., Pratsinis S.E.* Particle size distributions from small-angle scattering using global scattering functions // *J. Appl. Cryst.* - 2004. - Vol. 37. - P. 523 - 535.

Л. А. Булавін^{1,2}, О. В. Томчук^{1,3}, М. В. Авдєєв³

¹ Київський національний університет імені Тараса Шевченка, Київ

² Інститут проблем безпеки АЕС НАН України, Київ

³ Об'єднаний інститут ядерних досліджень, Дубна, Росія

ДОСЛІДЖЕННЯ БУДОВИ КЛАСТЕРІВ У ВОДНИХ СУСПЕНЗІЯХ НАНОАЛМАЗІВ МЕТОДОМ МАЛОКУТОВОГО РОЗСІЯННЯ НЕЙТРОНІВ

Представлено результати дослідження структури різних типів рідинних систем «вода - детонаційний нааноалмаз», які отримано за допомогою методу малокутового розсіяння теплових нейтронів. Було показано, що в діапазоні масових часток (0,3÷1,8) % експериментальні спектри добре описуються дворівневою моделлю універсального експоненційно-степеневого наближення. Отримані структурні параметри дозволили оцінити числа агрегації в досліджуваних системах. Знайдено розміри нааноалмазних частинок та їхніх кластерів, а також фрактальну розмірність останніх.

Ключові слова: детонаційні нааноалмази, малокутове розсіяння нейтронів, фрактальні кластери, число агрегації.

Л. А. Булавин^{1,2}, А. В. Томчук^{1,3}, М. В. Авдеев³

¹ *Киевский национальный университет имени Тараса Шевченко, Киев*

² *Институт проблем безопасности АЭС НАН Украины, Киев*

³ *Объединенный институт ядерных исследований, Дубна, Россия*

ИССЛЕДОВАНИЕ СТРОЕНИЯ КЛАСТЕРОВ В ВОДНЫХ СУСПЕНЗИЯХ НАНОАЛМАЗОВ МЕТОДОМ МАЛОУГЛОВОГО РАССЕЙЯНИЯ НЕЙТРОНОВ

Представлены результаты исследования структуры разных типов жидкостных систем «вода - детонационный наноалмаз», которые получены с помощью метода малоуглового рассеяния тепловых нейтронов. Было показано, что в диапазоне массовых долей (0,3÷1,8) % экспериментальные спектры хорошо описываются двухуровневой моделью универсального экспоненциально-степенного приближения. Полученные структурные параметры позволили оценить числа агрегации в исследуемых системах. Найдены размеры наноалмазных частиц и их кластеров, а также фрактальная размерность последних.

Ключевые слова: детонационные наноалмазы, малоугловое рассеяние нейтронов, фрактальные кластеры, число агрегации.

Надійшла 02.04.2015

Received 02.04.2015