O.A. KYZYMA,[1, 2] A.V. TOMCHUK,[1, 2] M.V. AVDEEV,[2] T.V. TROPIN,[2]
V.L. AKSENOV,[3, 2] M.V. KOROBOV[4]

[1] Taras Shevchenko National University of Kyiv
  (2, Academician Glushkov Ave., Kyiv 03022, Ukraine)
[2] Joint Institute for Nuclear Research
  (6, Joliot-Curie Str., Dubna 141980, Russia)
[3] B.P. Konstantinov Petersburg Nuclear Physics Institute
  (Orlova Roscha, Gatchina 188300, Leningrad district, Russia)
[4] Lomonosov Moscow State University
  (1, Leninskie Gory, Bld. 3, Moscow 119991, GSP-1, Russian Federation)

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STRUCTURAL RESEARCHES
OF CARBONIC FLUID NANOSYSTEMS

The results of researches concerning the cluster state in a number of disperse carbonic materials that are widely used in modern applications, including fullerenes and detonation nanodiamonds, are reported. With the help of the small-angle neutron scattering (SANS) method, some basic aspects of clustering in such systems are elucidated. At the same time, for the most effective and reliable description of a cluster structure under various conditions, a complex analysis involving complementary experimental and calculation techniques is applied. The experimental aspects of SANS applications are emphasized, and a qualitatively new idea of the structure of analyzed systems is formulated.

K e y w o r d s: fullerenes, nanodiamonds, small-angle neutron scattering.

1. Introduction

The interaction of various carbon forms (fullerenes [1, 2], nanotubes [2], nanodiamonds [2, 3]) with various solvents is a challenging problem directly associated with the application of the indicated systems in modern nanotechnologies, in particular, in biomedical applications. For instance, a possibility to apply fullerenes – highly symmetric C_{60} and C_{70} molecules – and their complexes in medicine has been actively studied in recent years [4–7]. Fullerenes also demonstrate strong antioxidative properties [8–12], which stimulates the development of their therapeutic use, e.g., at the treatment of neurodegenerative diseases. Some derivatives of fullerenes reveal an inhibition activity with respect to immunodeficiency virus

proteases and are proposed to be used for the suppression of the virus activity [13]. An antineoplastic activity of photo-excited fullerene derivatives was reported [14–17]. An almost spherical structure of the C_{60} molecule together with its size (about 1 nm) makes it possible to use fullerenes in the struggle with the flu virus by creating purely mechanical obstacles against the virus penetration into cells [18, 19].

It should be noted that the future advantage of applications of fullerenes gave rise to a considerable volume of their production in recent years, which invokes an issue concerning the ecologic safety and recycling [20, 21]. In this connection, extremely challenging are researches of the toxicity, structure, and stability of fullerene solutions, in particular, under the action of environmental salts [22].

A natural requirement for the applications indicated above to be implemented into practice is the

a

b
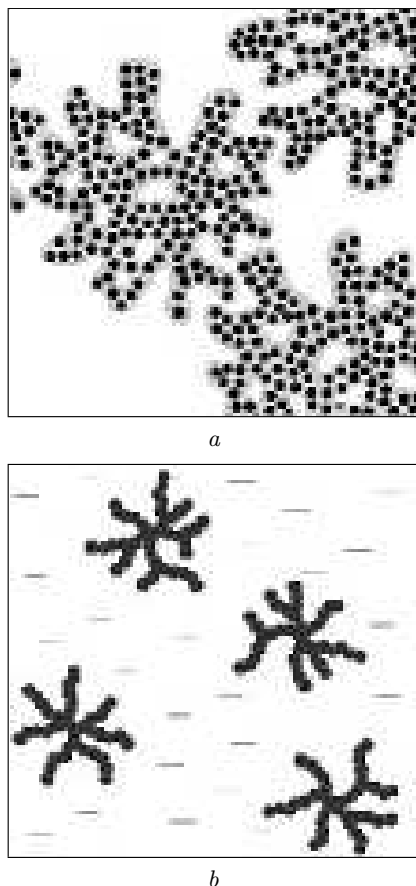
Structure of detonation nanodiamond clusters on a scale of 1–100 nm: powder (*a*), suspension (*b*)

availability of steady and controllable liquid systems containing fullerenes. However, as a whole, the modern structural researches testify to a complicated behavior of fullerenes and their derivatives in solutions, which is associated with the formation of clusters (aggregates) [23]. The study of clustering in such solutions needs a complex approach and a detailed study of solvents of various classes and under varios external conditions. The modern understanding of the problem of fullerene clustering in solutions, the formulation of actual problems, and the review of their solutions were analyzed in works [24–26].

Detonation nanodiamonds emerge, when a mixture of explosives unbalanced in oxygen is exploded in the absence of any other source of carbon [27, 28]. They are ultra-fine crystallites of cubic diamond. Their typical dimension determined by analyzing the width of diffraction peaks is about 4 nm [27–29]. Detonation

nanodiamonds are an attractive material from the application viewpoint. The prospects of their use include such domains of modern nanotechnologies as high quality polishing [30], electrode coating [31], nanocomposites [32–34], thin films [35, 36], and biomedical applications [37, 38]. However, the problem of nanodiamond cleaning is of concern. The main obstacle is the formation of rather robust aggregates. According to the modern view [39–44], nanodiamond powder is a conglomerate of aggregates with various dimensions, whose cores contain a highly stable complex of sintered diamond crystallites with dimensions ranging from 60 to 200 nm. Such robust structures were proposed [44] to call "agglutinates" (Figure, *a*).

Recently [44, 45], a method for the destruction of agglutinates in nanodiamond powders has been elaborated. It includes the powder mixing in special grinders containing micron-sized zirconium balls (a diameter of 30 μm) in a liquid medium. As a result, stable liquid dispersions of nanodiamonds are obtained. A capability of the complete deaggregation of nanodiamonds, as well as the dispersion of separate crystallites into the solution, was reported [3, 44, 46]. However, due to their large free surface, those particles demonstrate a tendency to new clustering (Figure, *b*), which becomes considerably stronger at relatively high concentrations of a dispersed material (> 1 wt.%) [44]. Water and polar non-aromatic solvents, such as dimethylsulfoxide (DMSO), are especially suitable liquids for the fabrication of required dispersions. At present, there is no definite opinion concerning the stabilizing mechanism of discussed dispersions.

In this work, various approaches to the solution of some problems dealing with the clustering in the solutions of fullerenes with different polarities and the dispersions of detonation nanodiamonds, including powders and suspensions on the basis of various solvents, are discussed. An important aspect of corresponding researches is the application of SANS in the framework of the complex approach, which combines a number of methods complementary to one another.

2. Results and Discussion

Unlike graphite and diamond, fullerenes are solvable in a wide class of solvents [23, 47, 48]. This property of fullerenes is associated [23] with their struc-

ture, which is strongly similar to that inherent to many organic solvents. A weak intermolecular bond in fullerene crystals, fullerites, in contrast to that in graphite and diamond ones, is another essential factor. Despite extensive experimental data on the solubility of fullerenes [47–51], nobody managed to introduce a generalized parameter, which would allow one to determine the saturation concentration for a given solvent on the basis of its parameters (polarizability, polarity, molecular size, energy characteristics, and so forth) [48]. Nevertheless, the influence of the solvent polarity can be singled out. The dipole moment of highly symmetric C_{60} molecules is almost equal to zero, which is responsible for the lyophobic character of the interaction between this fullerene and polar solvents. For instance, the saturation concentrations of C_{60} solutions in weakly polar liquids with the dielectric permittivity $\varepsilon < 10$ (toluene, benzene, carbon bisulfide, naphthalene) fall within the interval of 1–50 mg/ml (maximum C_{60} concentrations of 40–50 mg/ml are observed in naphthalene derivatives, such as dimethylnaphthalene, 1-chlornaphthalene, *etc.*). In polar solvents with $\varepsilon > 10$ (alcohols, pyridine, N-methylpyrrolidone (NMP)), the fullerene solubility is much lower and does not exceed 1 mg/ml. Concerning water ($\varepsilon \approx 80$), C_{60} molecules demonstrate a completely hydrophobic character (the solubility is less than 10^{-11} mg/ml). The latter fact is one of the main problems in biomedical applications of fullerenes. In order to insert C_{60} fullerene into water, various tricks are used, giving rise to the formation of colloidal solutions. In particular, a direct stabilization of fullerene in water is performed by its modification [52,53] or solubilization with the help of surfactants [54–57]. There are also ways of its indirect stabilization, e.g., the method of solvent change (the dispersion of molecular solutions of fullerene, in which the organic solvent does not mix with water, into water) [58–62]. In this case, dense aggregates appear, and fullerene molecules interact with water on their surface to form an electric double layer. However, the mechanism of this interaction is not sufficiently clear. There is the evidence [63] that a colloidal solution of non-modified C_{60} in water can be prepared with the help of the extremely long high-frequency and high-power ultrasound stirring of the aqueous suspension of fullerite.

As was mentioned above, low-polarity solvents (conditionally, $\varepsilon < 10$) dissolve fullerenes rather well.

The UV-Vis absorption spectra of those solutions demonstrate peaks that are typical of single fullerenes in gas [64, 65] and fullerenes in the crystalline state [1, 66, 67], but are shifted, with the shift depending on the solvent. The existence of a saturation limit for fullerenes in those solvents testifies to the molecular type of solutions.

However, molecular solutions are not always stable. As was found in a number of experimental works, various clusters can be formed in them. Fullerene clusters were observed for C_{60} solutions in benzene [68–71], toluene [72, 73], and carbon disulfide [74–81]. As a principal cause of the clustering in low-polarity solutions, we consider nonequilibrium conditions occurring in the course of their preparation. Starting from the first works dealing with the solubility of fullerenes in various solvents [47], ultrasound or intensive mechanical agitation for a long time (up to several days) is used to enhance the dissolution, which can result in the solution supersaturation. The solutions prepared under the conditions close to equilibrium were studied with the help of SANS [75, 82, 83]. Powder of C_{60} fullerene was added to carbon disulfide, and the mixture was left at rest for three days at a constant temperature of 25 °C till the complete dissolution of fullerene. SANS measurements did not detect clusters discussed above, which definitely indicates the role of preparation conditions of fullerene solutions in the clustering. In order to study the solvent structure around a C_{60} molecule, molecular dynamics calculations were carried out [75, 84]. As a result, a concept of small clusters was proposed [75, 83], in which some fraction of dissolved fullerene molecules were assumed to form dimers.

In low-polarity solvents, the formation of fullerene clusters is governed by the conditions of solution preparation. At the same time, in the case of polar solvents (conditionally, $\varepsilon > 10$), experimental data unambiguously testify to the clustering after a certain period after the dissolution. A typical time of cluster growth amounts to weeks and months. In this case, the size of clusters reaches submicronic dimensions and afterward remains stable (for a year or longer). Such clusters of C_{60} molecules were observed in various nitrogen-containing solvents: pyridine [85], N-methylpyrrolidone (NMP) [86], benzonitrile [71], and benzene–alcohol mixtures [71, 87]. As a whole, the solubility of fullerenes in polar solvents is lower than in low-polarity ones. Therefore, the influence of

the solvent polarity on the clustering is studied in the mixtures of low-polarity and polar solvents [71, 86–91]. By varying the volume fraction of the polar component, the dielectric permittivity can be changed in a wide range. It was noticed that the C_{60} clustering begins in mixtures with $\varepsilon^0 > 13$ [71]. For C_{60} solutions, this threshold is much higher, $\varepsilon^0 > 27$ [91].

In a number of polar fullerene solutions, the temporal solvatochromic effect is observed, i.e. the smoothing of characteristic peaks in the UV-Vis spectra of solutions in the course of the time. In works [85, 92–96], this effect was associated with the clustering. In particular, in work [85], the smoothing of the UV-Vis spectrum in polar solutions was supposed to result from the enhancement of the Rayleigh scattering by clusters. However, the peak disappearance against a low increase of the total absorption cannot be explained as an addition of some background of the power-law type, as well as by corrections to the Rayleigh law (analogous to Mie scattering) associated with cluster dimensions [96].

The modification of the characteristic peak at 330 nm can be connected with a change of the C_{60} state in the solution. This peak is observed for all fullerene states: gas, molecular solution, and crystals [65]; it also corresponds to certain transitions between electron levels. However, it decreases substantially at the fullerene crystallization. An inverse phenomenon is observed at the evaporation of C_{60} crystals [97]. From whence, it follows that a decrease of the peak at 330 nm in the spectrum of C_{60}/NMP solution in time effectively reflects the transition of fullerene from the molecular state to the cluster one, for which molecular forces (the van der Waals bond) are responsible.

Another possible reason for a change of the spectrum under discussion is a specific interaction between the dissolved fullerene and the solvent. In works [98–100], C_{60} was concluded to be a good electron acceptor and to form complexes with charge transfer, which can be regarded as a probable source of the temporal solvatochromic effect [92–94].

In order to elucidate the role of each mechanism in the temporal solvatochromic effect observed in the C_{60}/NMP system, a complex structural research was carried out. Its results testify that, first, being extracted from the C_{60}/NMP solution, fullerene can transform into a nonpolar phase only in the molecular state [101], and, second, almost all fullerenes trans-

form into the cluster state in the solution C_{60}/NMP in the course of the time. The transition in time from the molecular solution into the colloid one in the C_{60}/NMP system was studied in detail, by using the mass spectroscopy [102–104] and IR-spectroscopy [105] methods. The growth of fullerene clusters in those systems was described on the basis of kinetic equations from the nucleation theory [106–110].

The additional research of the dilution of fullerene solutions in polar solvents by other solvents made the situation substantially clearer. For instance, the addition of water to the system C_{60}/pyridine (till the total mixing with pyridine) is accompanied by the strong solvatochromic effect [85, 111]. In this case, clusters with considerably smaller dimensions (several tens of nanometers) than in the initial solution were observed in the mixed system [111]. If water was added to the C_{60}/N-methylpyrrolidone system, the solvatochromic effect was a little weaker [95]. Similar effects were shown [85, 95, 112] to have a critical character: they become pronounced only after a certain quantity of water was added (to 40–50 vol.% in terms of the final solution). Clusters in NMP are close-packed formations with insignificant (less than 10 vol.%) probable inclusions of hydrogen-containing molecules [112]. In further works [95, 96, 102, 104, 113, 114], the mechanism of this reorganization was determined. Namely, the addition of water stimulates the detachment of separate C_{60} molecules from the clusters, which results in an effective reduction of the number of clusters.

Combining the analysis of two mechanisms driving the temporal solvatochromic effect in polar C_{60} solutions, we draw conclusion that the both processes discussed above give contribution to this effect. In the course of the fullerene dissolution in the polar solvent, a molecular solution is formed first, which transforms in time into a colloidal solution, where fullerene is mainly in the cluster state. Simultaneously, the bond in the C_{60}–MNP complex changes. We believe that the last modification is responsible for the stabilization of large clusters in this solution.

Polar solvents like nitrogen-containing solvents with aromatic rings in their structure can be mixed well with low-polarity solvents. The addition of such solvents, e.g., into the C_{60}/MNP solution also results in the cluster reduction [115]. In order that the effect manifest itself, a certain amount of toluene should be added (to more than 50 vol.% in terms of the final

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solution) [116, 117]. In this case, the transition into the molecular state can be explained by the natural solubility of C_{60} in the added solvent.

Hence, a conclusion can be drawn that the temporal solvatochromic effect in polar solvents is not a consequence of the clustering only, but it takes place simultaneously with the clustering as a result of the donor-acceptor complex formation. The inseparable character of the cluster and complex formation processes has to be emphasized, because the formation of donor-acceptor complexes affects the solubility and the stabilization of fullerene in the solution.

Aqueous colloidal solutions of C_{60} fullerene compose a special class of C_{60} solutions that are interesting from the viewpoint of biomedical applications. The idea of the insertion of C_{60} into water by changing the solvent [58–60, 62] was briefly characterized above. The maximum achievable concentration of C_{60} in the colloidal solution amounts to approximately 1.6 mg/ml, which is comparable with the solubility of fullerene in aromatic solvents, e.g., in benzene (1.5 mg/ml). The obtained dispersions remain stable for a long time interval (not less than 12 months). The characteristic size of fullerene clusters amounts to 70 nm [61, 62, 118–121]. SANS testifies to a certain elongation of clusters, which was explained as a result of the minor secondary aggregation: initial clusters about 10 nm in dimensions join to form small associates (the aggregation number is less 10) with a characteristic dimension slightly more than 72 nm. A similar conclusion was also made for C_{60}/pyridine/water solutions. In work [122], a possibility to model the distribution function of aggregates over their dimensions in the case of C_{60} aqueous solutions was analyzed.

The internal structure of clusters and particles composing them was actively discussed in the literature. At first, the authors of the dispersion method [59] assumed that fullerene, while interacting with water under the preparation conditions, forms C_{60}/H_2O complexes, which aggregate into clusters. The second possible structure corresponds to the crystallization. At last, the third type of a structure was discussed in connection with the data of differential scanning calorimetry [119]; namely, at the water evaporation from the solution, an additional peak was observed, which corresponded to the "closed" water freezing at a temperature of −2.3 °C. According to SANS data obtained with the help of the contrast

variation [120], the most preferable is the simplest case of the fullerene crystallization. The stabilization of such clusters occurs owing to the fullerene hydroxylation [123].

In works [62, 121], the structural features of aqueous colloidal solutions of fullerene C_{60} fabricated by various manufacturers were compared. The detection of the solution dispersion dependence on the ultrasound application time at the dispersing became important for practical usage. Structural features of the coagulation of the solutions concerned were studied in work [121] taking advantage of the combination of visible and ultra-violet radiation spectroscopy and small-angle neutron scattering. Numerous structural researches of aqueous fullerene solutions were started owing to the fact that the dimensions of fullerene aggregates in the system determine their biological properties, first of all, toxicity [124, 125], which make them a promising object for medical and biological applications.

Small-angle neutron scattering was also used to reveal structural features in the powders of detonation nanodiamonds [126] and their suspensions [127–131, 134]. Within a considered interval of dimensions, a well-pronounced two-level organization was observed: the level of nanodiamonds and the level of their fractal clusters.

While studying the powders of detonation nanodiamonds, their fractal structure was found to possess a lower fractal dimensionality, if higher pressures were applied in the course of their preparation. This observation stimulated a research [126], where identical already synthesized nanodiamond powders were subjected to various static pressures up to 1000 MPa. The pressure expectedly induced changes in the fractal structure of the powders, which were analyzed in the course of experiment. The reduction of the mass fractal dimensionality in clusters from 1.8 (before the pressure was applied) to about 1, as the pressure grew, gives an argument in favor of the scattering at pores located between densely packed crystallites (Figure, *a*). The inertia radius of nanodiamond crystallites in the initial powder was 27 Å and changed to 23.5 Å after the pressure was applied. The obtained initial radius is a little larger in comparison with the value given by X-ray diffraction. This fact testifies to the existence of an additional component on the nanodiamond surface, which determines the difference between the size seen in

SANS" and the "crystal" one. The binding into clusters in nanodiamond powders occurs owing to the existence of a non-diamond shell (graphene) on the crystallite surface. The presented data testify that this shell is inhomogeneous and has a diffusive character [130]. Under pressure, this shell changes a little toward a smooth surface. This implies that the pores do not disappear only; they appear as well, but with a slightly smoothed surface. Nevertheless, the recombination of pores prevails, which manifests itself as a reduction of the fractal dimensionality. Hence, the revealed effects point to three important facts. First, the powders of detonation nanodiamonds are porous systems. Second, the nondiamond shell around nanodiamond crystallites has an inhomogeneous diffusive structure. Third, under the action of moderate pressures, nanodiamond crystallites can move in the structure of clusters, with an effective reduction of the nondiamond shell. Those facts promote the application of the nanodiamond powder grinding in liquid media for the separation of powders into nanocrystals and the following manufacture of nanocrystal suspensions.

The description of a structure in the suspensions of detonation nanodiamonds with the help of SANS [127] allowed a number of principal issues to be elucidated, which are important for the understanding of the dispersion mechanism of detonation nanodiamonds into liquid carriers [3, 46]. Concentrated liquid dispersions of detonation nanodiamonds in water and DMSO were studied. Experiments of two kinds were carried out. First, the interaction between clusters at the dissolution of initial systems was monitored. Second, the contrast variation was applied at the dissolution of initial systems by the corresponding mixtures of H- and D-solvents. The scattering was close for two suspension types. The characteristic dimension of clusters was evaluated to equal about 40 nm. The diffusive character of inhomogeneities on the surface of nanodiamonds was also confirmed. As in the case of powders, the new clusters in liquid dispersions turned out to be mass fractals with a dimensionality of 2.3–2.4. The fractal nature of examined clusters was discussed in terms of the unique mechanism of their growth, which is close to the diffusion-limited aggregation throughout the whole growth process [129, 131].

The structural factor that appears as a result of the cluster-to-cluster interaction is well detected in con-

centrated specimens. The concentration dependence of the scattering confirms the repulsive character of interaction between clusters. The corresponding correlation length becomes smaller than the characteristic cluster dimension at a high cluster concentration, which testifies to a mutual penetration of branched cluster structures. The contrast variation experiments confirm this concept and also evidence the presence of a nondiamond component. The presence of graphene at interfaces manifests itself in various spectroscopic data (UV-Vis, Raman, XANES, and FTIR spectra) [132], as well as in EPR and NMR spectra [133]. In work [127], the fraction of the graphene component in a composition of nanodiamonds was evaluated in the framework of the monodisperse approximation for the "core–shell" model. Assuming the shape of crystallites to be spherical, a value of 3.9 nm was obtained for the total particle radius. In view of the observed radius of nanodiamonds, this value corresponds to a graphene shell 0.5 nm in thickness. If polydispersion is taken into consideration, a little smaller thickness of the shell is obtained, namely, 0.4 nm.

In work [130], a detailed analysis of SANS by particles with diffusive surface was carried out, with detonation nanodiamonds being taken as an example. The case of a low surface diffusivity was considered in detail, which made it possible to analyze the structure of nanodiamonds in terms of a continuous radial profile of the power-law type; the latter describes well the carbon transition from the diamond state in crystallites to the graphite state on the surface [134]. This concept considerably simplified the analysis of both the polydispersion and changes of the scattering invariants at the contrast variation. The distribution of particles over their sizes was analyzed in the log-normal approximation and gave the average size of nanodiamond particles equal to about 3 nm for all the systems concerned at a dispersion degree of 35–40%. The SANS method was also applied to study the structural features in the light and heavy fractions of nanodiamond suspensions separated with the help of centrifugation [131].

A high stability of clusters in liquid systems has to be pointed out, the mechanism of which has not been completely understood. This mechanism has an electrostatic character, because the dispersions coagulated, when salts were added [3]. The stabilization of nanoparticle dispersions was associated [46] with

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the particle–solvent interaction; in particular, the appearance of a solvation shell owing to hydrogen bonds was supposed. In work [127], the appearance of this phase was associated with the developed structure of clusters in dispersions. At drying, clusters start to strongly overlap one another. As a result, there emerge pores filled with the solvent, and the evaporation from those pores is complicated.

3. Conclusions

Hence, the variety of methods used in structural researches promotes the reliable adequate elucidation of the structure in carbon nanosystems. Their comprehensive study allowed us to clarify the relations between the solvatochromic effects and the cluster state of fullerene in organic solvents, as well as the features of cluster formation and reorganization in solutions with various polarities and in their mixtures, when the system polarity, time, and preparation conditions change.

A progress in the synthesis of highly stable and concentrated aqueous carbon nanosystems has to be emphasized. The structure of colloidal C_{60} solutions in water prepared with the use of the method of solvent change is determined. The applied preparation procedure was shown to possess a good reproducibility. In addition, the influence of salt additives on the solution structure was determined. The method of small-angle neutron scattering together with a number of complementary techniques was successfully used for the specification of a cluster structure in highly disperse materials on the basis of detonation nanodiamonds. For nanodiamond powders, the modification of their porous structure under the action of an external pressure was revealed. The existence of a nondiamond (graphene) shell, which is responsible for the break of the anchoring between crystallites and their agglomerates under the pressure action, is proved. The strong clustering is demonstrated to take place in liquid dispersions of detonation nanodiamonds in various polar media. The branched structure of clusters making their mutual penetration possible is proposed.

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О.А. Кизима, О.В. Томчук, М.В. Авдєєв,
Т.В. Тропін, В.Л. Аксьонов, М.В. Коробов

СТРУКТУРНІ ДОСЛІДЖЕННЯ
РІДИННИХ ВУГЛЕЦЕВИХ НАНОСИСТЕМ

Р е з ю м е

Основною метою представлених досліджень є вивчення кластерного стану низки дисперсних вуглецевих матеріалів, які є актуальними на сьогодення, включаючи фулерени, та детонаційні наноалмази. За допомогою малокутового розсіяння нейтронів (МКРН) висвітлено ряд принципових аспектів кластероутворення у наведених системах. Разом з тим, для найбільш ефективного та надійного опису структури кластерів за різних умов, застосовується комплексний аналіз із залученням комплементарних експериментальних та розрахункових методів. Виділено експериментальні аспекти застосування МКНР, які дозволили отримати якісно нове представлення про структуру досліджуваних систем.