

Modeling of Carbon Nanostructures Synthesis in Low-Temperature Plasma

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Abstract

The article discusses approaches to constructing mathematical models describing processes in a low-temperature plasma with different levels of detail of elements. The areas of application, limitations and computational complexity of various methods for modeling collective processes in multicomponent plasma are shown. Using the example of electric arc synthesis, the mechanism of formation of carbon nanostructures (fullerenes, nanotubes) in plasma is considered, taking into account the formation of carbon cluster groups with C—C, C=C (C₂) and C—C=C (C₃) bonds. The quantum-kinetic approach to constructing a mathematical model using the Boltzmann kinetic equation for the synthesis of carbon nanostructures (CNSs) using the method of sublimation of graphite raw materials by arc plasma is considered. The use of the distribution functions of particles allows considering the processes of formation and growth of cluster groups in plasma. Modeling plasma processes is a resource-intensive task associated with processing large amounts of data. Therefore, to reduce the amount and time of computation, it is proposed to use the method of large particles for the numerical solution of model problems. The organization of distributed parallel computing on a CPU and a GPU also makes it possible to reduce the total time for solving the problems of a model describing the CNS plasma synthesis processes. The article presents the results of compliance of the developed model with the physical process of the CNS synthesis. The study of the numerical characteristics of particle collisions and the formation of cluster groups C₂ and C₃ along the length of the plasma interelectrode space has been carried out. The analysis of the results showed that the number of collisions and the formation of cluster groups depends on the concentration, velocity and particle size. The developed model allows us to investigate the characteristics and properties of the processes of formation, various CNS in the plasma, taking into account the characteristics of the synthesis.

Keywords

Mathematical model; carbon nanostructures; plasma.

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Introduction

A feature of carbon is its unique ability to form various stable covalent bonds between atoms. This allows him to create multiple allotropic forms or modifications that differ in the structure of the crystal lattice and properties. Conventionally, all the basic and transitional allotropic forms of carbon can be represented in the form of the tertiary diagram shown in Fig. 1 [1]. The main forms of carbon are at the vertices of the triangle, while the transitional forms are on the sides and inside.

Possessing a set of unique physical and chemical properties and a small size, fullerenes and nanotubes are considered to be promising materials for modern industry. The introduction of the designated carbon

nanostructures (CNSs) into the matrix of polymer resins in the amount of 0.01–5 % by weight makes it possible to create composite materials with new or improved properties (increased rigidity and dimensional stability, thermal conductivity, fire resistance, electrical conductivity, etc.), which is of interest for various branches of the national economy. The atomic structure of the CNS is a set of related pentagons P and hexagons H formed by cluster groups with C—C, C=C (C₂) and C—C=C (C₃) bonds. Depending on the P/H ratio of the hybridization located on the sp^2 – sp^3 side (Fig. 1), a certain structure of the C_x series fullerene is formed. At the ratio $P/H \rightarrow 0$, which corresponds to the sp^2 hybridization, graphene is formed, and at the ratio $P/H \rightarrow \infty$, the

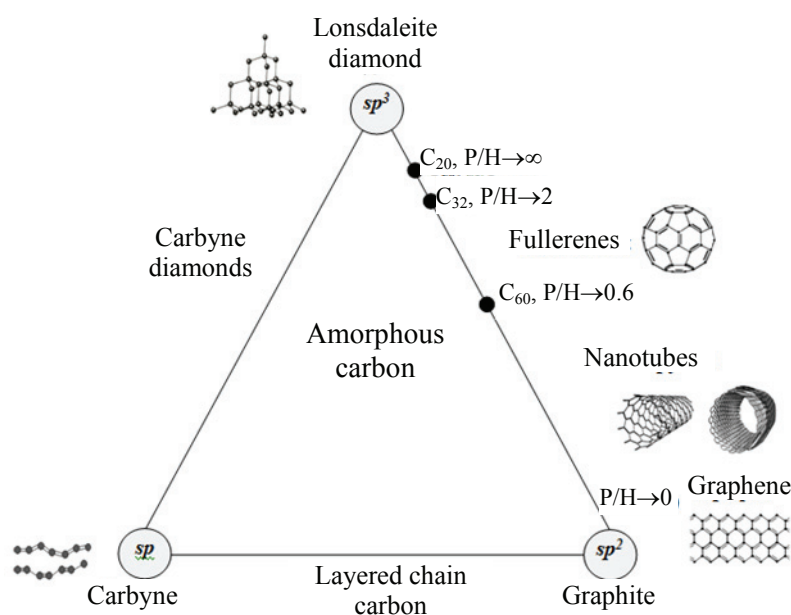


Fig. 1. Tertiary diagram of allotropic forms of carbon

diamond-like C_{20} is formed. As can be seen from this diagram, the number of P/H ratios determines the structure and, accordingly, the properties of the CNS.

The widespread use of CNSs in various areas of industry is constrained by their high cost and low productivity of the existing synthesis methods [2]. This is due to poor knowledge of the theoretical foundations of the formation processes. Currently, there is no consensus on the model of carbon atoms grouping into clusters, with the subsequent formation of various bulk nanostructures. Understanding of mechanisms and conditions of the CNS formation at the cluster level makes it possible to make purposeful improvements to the existing technologies and create new ones, to modify the methods and conditions of synthesis, thus increasing the efficiency of industrial production.

The study of methods and the search for optimal conditions for the synthesis of CNS by experimental methods is inefficient and quite complicated; therefore, it is more practical to use methods of mathematical modeling. The problem of modeling complex processes of the CNS formation at the stage of formation and growth of cluster carbon groups is a challenging and resource-intensive task.

Currently, a large number of technologies for the synthesis of CNS differing in the ways of conducting the process, the structure of the final product, the quantity and quality of the nanomaterial, the ability to scale, have been developed [3]. Conventionally, all the well-known synthesis methods that can be used for the industrial production of CNSs can be divided into two groups: pyrolysis of carbon-containing gas processes

and sublimation-desublimation of graphite raw materials. Each of these methods has its own characteristics, with a number of factors affecting the process and properties of the resulting product, as well as its inherent drawbacks. Practically in all technologies of the CNS synthesis, thermal destruction of the initial structure of carbon-containing material initially occurs with condensation of carbon vapors at the final stage of the process. One of the well-known varieties of CNS production methods is plasma synthesis [4]. Modern technologies of plasma synthesis allow creating a high-quality product with a large proportion of yield, using significant amounts of graphite raw materials and conducting the process continuously, which is necessary for industrial production [5].

Plasma synthesis involves the process of producing CNS in a low-temperature arc discharge plasma in an inert gas medium [6].

The use of various catalysts allows achieving a yield of up to 90 % of the raw materials used. This technological process is characterized by a high concentration of energy in a small region of space, rapidity, as well as a large number of different effects of interaction of different particles during phase and structural transformations, the influence of a significant number of factors on the final product. A distinctive characteristic of the process is the small length of the interelectrode synthesis zone, in which a low-temperature plasma is formed with a temperature of about 4200–5500 K. At the same time, in the plasma space, there is a huge number of particles, which move at a speed of 3000–6000 m/s and interact with each other under the action of the electromagnetic field.

The indicated number of features of producing CNSs by the plasma method complicates the empirical studies of the synthesis characteristics and increases the relevance of using modern tools for mathematical modeling for complex, resource-intensive processes occurring in the CNS synthesis.

The purpose of this research is to study the approaches and develop a method for mathematical modeling of the plasma synthesis of CNS by the graphite sublimation, which allows describing the formation and growth of cluster carbon groups with various types of bonds in a low-temperature plasma forming bulk structures. The study of the formation of cluster groups in plasma allows for the evaluation of the characteristics and properties of the CNS synthesis processes without conducting full-scale experiments.

Methods of mathematical modeling of processes in plasma

Technologically, the CNS synthesis methods based on the thermal evaporation of graphite by the arc discharge plasma in an inert gas medium are similar to the process of electric arc welding. However, the conditions of synthesis, the flow of processes in plasma with the presence of buffer gas atoms and a catalyst, the sublimation of graphite raw materials and the condensation of carbon particles on the cooled chamber elements, significantly distinguish this method of producing CNSs by the electric arc welding process. The application of the fundamental laws of physics and chemistry to simulate nano-objects and processes characterizing plasma synthesis of CNSs is complicated by the fact that many interacting phase and structural transitions with certain features occurring simultaneously in plasma are often impossible to separate. Therefore, the existing mathematical models cannot be applied to describe these processes.

For mathematical modeling of the processes occurring in plasma during the CNS synthesis, it is

possible to use models of different levels of hierarchical detailing, differing in the accuracy of the object description, the possibilities of accounting for the process specifics and computational costs in the numerical solution (Fig. 2).

Conventionally, all methods for modeling processes in plasma can be divided into classical, semi-classical, and quantum mechanical [7]. Classical models allow nanosystems to be modeled with low computational costs, but show low accuracy of simulation results and do not allow describing the processes of interaction and the formation of nanostructures [8]. The use of semi-classical models provides an acceptable compromise between computational costs and the accuracy of describing physical phenomena in plasma, but does not allow investigating the processes of formation, growth, and interaction of nanostructures at the atomic level [9]. The use of the quantum-mechanical approach gives a high accuracy of the apparatus used when describing physical phenomena in plasma, but creates difficulties in constructing a model and requires very large computational costs for a numerical solution [10].

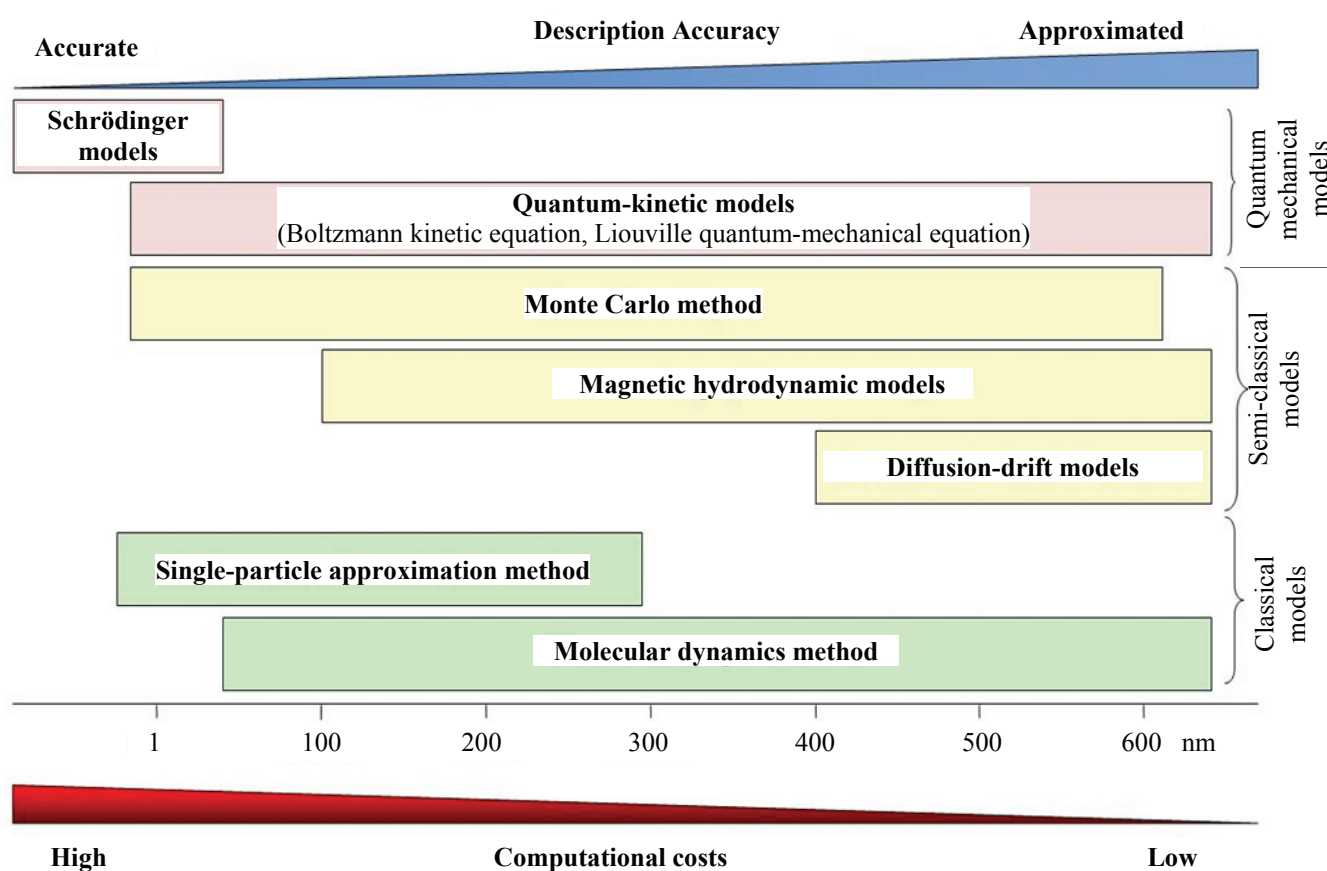


Fig. 2. Methods of mathematical modeling of CNSs

At present, it is the physical limitations of a classical computer that hinder the wide use of such models for modeling plasma processes and their use in engineering practice. However, the use of quantum-kinetic models for describing the motion and interaction of particles in plasma makes it possible to obtain simpler ones as compared to the Schrodinger ones. They allow one to describe nanostructures in plasma in a wide range of linear dimensions.

Models based on the methods of single-particle approximation and molecular dynamics are models of traditional classical approaches describing processes in plasma. The one-particle approximation method corresponds to the Lagrange approach, when the trajectory of a particle moving in plasma with respect to a given coordinate system is considered. In this method, each charged particle is considered separately, not affecting other particles and on external conditions. For the plasma discharge arc, the motion of a particle of mass m and charge q in an electromagnetic field is described by the equation:

$$m \frac{d^2 \vec{r}}{dt^2} = q \left(\vec{E} + \frac{1}{C} \vec{\mathfrak{G}} \vec{H} \right), \quad (1)$$

Equation (1) is reduced to a system of two equations written in the form:

$$\begin{cases} \frac{d\vec{r}}{dt} = \vec{\mathfrak{G}}, \\ \frac{d\vec{\mathfrak{G}}}{dt} = \frac{q}{m} \left(\vec{E} + \frac{1}{C} \vec{\mathfrak{G}} \vec{H} \right), \end{cases} \quad (2)$$

under initial conditions $t = 0$: $\vec{r}(0) = \vec{r}_0$, $\vec{\mathfrak{G}}(0) = \vec{\mathfrak{G}}_0$.

Here $\vec{E}, \vec{H}$ are electric and magnetic field strength vectors; $\vec{\mathfrak{G}}$ is particle velocity field; $\vec{r}$ is particle coordinates; C is light speed.

The system of equations (2) can be represented as a developed system consisting of six equations: three for the coordinates and three for the velocity components. In the end, we obtain a system of equations consisting of six Cauchy problems and with six initial conditions.

A significant disadvantage of this modeling approach is the limited conditions for its applicability. It is mainly used to consider processes in discharged plasma, where the effects of charged particles on each other are not taken into account. In the calculation of the motion of charged particles with this approach, only external electromagnetic fields are taken into account, which are not related to the flow of moving charged particles and their interactions. The one-particle approximation method may be used to

calculate the focusing of beams, plasma confinement areas, but it cannot be used to simulate processes in the arc discharge plasma.

To build mathematical models that describe dynamic processes in plasma, when it is necessary to take into account the collective interaction of individual particles, you can use the molecular dynamics method (MDM). The essence of MDM lies in the numerical solution of a system of N equations describing the motion of particles taking into account their interaction. Given that each of the N particles interacts with $N-1$ particles, then the total number of required calculation operations will be proportional to the square of the number of all N^2 particles. At each time step, it is necessary to calculate the position of each particle and calculate all N^2 interactions of particles. Such an approach, even for the modern stage of development of computing technology, as applied to the modeling of processes in plasma, is a rather laborious and resource-intensive task due to the processing of very large amounts of data.

When constructing a plasma model using an MDM system of equations describing the motion of the i -th particle and its interaction will have the form:

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}(\vec{r}_i) - \sum_{j \neq i} \nabla U_{ij}(\vec{r}_{ij}), \quad (3)$$

where U_{ij} is interaction potential of the i -th and j -th particles; $\vec{F}(\vec{r}_i)$ is external force.

The force acting on a charged particle in an electromagnetic field will be:

$$\vec{F}(\vec{r}_i) = Z_i e \left(\vec{E} + \frac{1}{C} \vec{\mathfrak{G}}_i \times \vec{H} \right), \quad (4)$$

The interaction potential between charged particles is determined by the charges of the particles and the distance between them:

$$U_{ij} = \frac{Z_i Z_j e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (5)$$

where Z_i and Z_j are multiplicity of charges of the i -th and j -th particles.

The use of the MDM involves the observance of certain requirements for the model:

1. The equations of motion of particles (3) must be integrated with a sufficiently small step, which is significantly less than the time of collisions of particles.

2. Consideration of the dynamics of processes in plasma requires a transition to statistical quantities – density and particle distribution functions.

3. It is necessary to specify the initial state of the components of the system under consideration, which is determined by the initial distribution of all particles.

In addition to the large amount of computation in the MDM, it has some methodological limitations for modeling processes in plasma. Each particle appears to be a kind of chemically inert bead, for which it is possible to use only one type of Coulomb interactions. The interaction of particles is determined by the distance between them and a strictly deterministic charge, which excludes any probability factor.

For mathematical modeling of low-temperature plasma processes, like arc processes, it is possible to use approaches based on the use of semi-classical models – the magnetic hydrodynamic description (MHD) and the Monte Carlo method.

The use of MHD descriptions for modeling processes in plasma allows considering it as a medium consisting of several types of different liquids. This approximation can be applied only in the presence of an equilibrium distribution of particles, using the Boltzmann distribution of particles. This condition is fulfilled when modeling cosmic plasma, plasma processes for plasma accelerators, etc. [11]

The system of equations describing the object in question will include a number of equations – those of continuity, motion, state for each plasma component, supplemented by Maxwell's equations, which describe the electromagnetic field and its relation to currents:

$$\begin{cases} \frac{\partial n_\alpha}{\partial t} + \operatorname{div} n_\alpha \vec{\mathfrak{g}}_\alpha = 0, \\ m_\alpha n_\alpha \frac{\partial \vec{\mathfrak{g}}_\alpha}{\partial t} = -\nabla p_\alpha + Z_\alpha e n_\alpha \left(\vec{E} + \frac{1}{c} \vec{\mathfrak{g}}_\alpha \times \vec{B} \right), \\ p_\alpha = n_\alpha k T_\alpha, \\ \operatorname{div} \vec{E} = 4\pi e \left(\sum_{\alpha \leq e} Z_\alpha n_\alpha - n_e \right), \\ \operatorname{rot} \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}, \\ \operatorname{div} \vec{B} = 0, \\ \operatorname{rot} \vec{B} = \frac{4\pi}{c} \vec{j}, \end{cases} \quad (6)$$

where n_α is density of grade α particles; $\mathfrak{g}_\alpha$ is particle velocity; T_α is particle temperature.

In the system of equations (6) temperature T_α is defined as an external parameter. Adding the heat balance equation to (6) makes the system closed and for its numerical calculation it is necessary to specify only the initial and boundary conditions. However, the

use of this method for describing the processes of electric arc synthesis of CNSs does not make it possible to fully investigate the processes of formation, growth, and interaction of carbon cluster groups in the plasma of the interelectrode space.

For modeling of interaction of particles with something in plasma processes, when it is necessary to take into account the probabilistic nature of these interactions, the Monte-Carlo method (statistical test method) is used. This approach is based on the systematic use of a random number generator to determine the subsequent history of each particle involved in the calculation. The method of statistical tests is algorithmically simple to implement, but rather laborious in terms of machine time costs. The error of the method is inversely proportional to the inverse of the number of considered particles. Increasing the accuracy of calculation by an order of magnitude requires an increase in the number of particles by two orders of magnitude.

The limitation of using the Monte-Carlo method is also the need to find the probability of all the considered processes for a different range of particle energies, angles and interaction distances. These probabilities are empirical; therefore, they initially introduce a modeling error, which must be taken into account. When modeling by this method, when there are a large number of internal relationships, therefore, the solution of the model's problems can be unstable.

The use of a quantum-kinetic description is used to simulate such phenomena in plasma as transport, oscillations, interactions, instabilities, etc. With this approach, the behavior and interaction of particles in plasma is described by the time distribution function. For example, the solution of the Boltzmann kinetic equation [12] allows one to find the distribution functions of particles with allowance for collisions for a certain point in time. When considering collisions of particles, considerable difficulties arise with both the calculation of the collision integral on the right-hand side of the Boltzmann equation and the very numerical solution of the entire equation. The kinetic Boltzmann equation is written as:

$$\frac{\partial f}{\partial t} + \vec{\mathfrak{g}} \frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{m} \frac{\partial f}{\partial \vec{r}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}, \quad (7)$$

where $f(\vec{r}, \vec{\mathfrak{g}}, t)$ is the particle distribution function; $\vec{F}$ is the force acting on the particle; m is the particle mass.

The collision integral in equation (3) has the form:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \iint (f' f'_1 - f f_1) |\mathbf{g}_1 - \mathbf{g}| d\sigma d\mathbf{g}_1. \quad (8)$$

Here $f f_1$ and $f' f'_1$ are particle distribution functions before the collision and after the collision, respectively; $\mathbf{g}, \mathbf{g}_1$ are particle velocities before and after collision; $d\sigma = \sigma d\Omega$ is differential effective cross section in solid angle $d\Omega$, dependent on the law of the interaction of molecules. When modeling particles in the form of rigid elastic spheres $\sigma = 4R^2 \cos \psi$, where R is the particle radius; ψ is the angle between the relative velocity of the colliding particles and the line connecting their centers.

When describing the plasma of particles charged without taking into account their collisions, the Boltzmann equation (3) is transformed into the Vlasov equation:

$$\frac{\partial f}{\partial t} + \vec{\mathbf{g}} \frac{\partial f}{\partial \vec{\mathbf{r}}} - q \left(\vec{\mathbf{E}} + \frac{1}{c} [\vec{\mathbf{g}}, \vec{\mathbf{B}}] \right) \frac{\partial f}{\partial \vec{\mathbf{p}}} = 0, \quad (9)$$

where $\vec{\mathbf{F}} = q \left(\vec{\mathbf{E}} + \frac{1}{c} [\vec{\mathbf{g}}, \vec{\mathbf{B}}] \right)$ is the Lorentz force; $\vec{\mathbf{p}}$ is the particle momentum field; $\vec{\mathbf{B}}$ is магнитная индукция.

The initial equations (7)–(9) must be supplemented with a system of Maxwell equations [13] to find the parameters of a self-consistent electromagnetic field.

Using the quantum Liouville equation to simulate plasma processes also involves using the many-particle particle distribution function f , which has the form:

$$\frac{\partial f}{\partial t} - iLf = 0, \quad (10)$$

where $iLf = \frac{1}{i\hbar} [f, H]$ is a quantum-mechanical Liouville operator; $i = 1, \dots, K$, ($K = 3N$); H is full Hamiltonian of the system; L is a linear Hermite operator; $\hbar$ is the Planck's constant.

The Liouville equation (10) determines the time variation of the distribution function of the Hamiltonian system in the phase space. It allows one to describe the motion of phase points in the $6N$ -dimensional phase space and to find the statistical operator for any time instant, if it is known at the initial time instant. The application of the Liouville equation to describe processes in arc discharge plasma is extremely difficult and requires very large computational resources.

The construction of models of atomic molecular systems can also be carried out within the framework

of Schrodinger models based on the use of wave functions of the probability distribution. The description of wave propagation makes it possible to determine the probability of finding a particle at a given point in space. Hamilton's operator of such models includes the kinetic energies of nuclei and electrons, the potential energy of the Coulomb interaction between nuclei, electrons, and between nuclei and electrons and has the form:

$$H = \frac{1}{2} \sum P_n^2 / M_n + \frac{1}{2} \sum p_i^2 / m + \frac{1}{2} \sum e^2 (|r_i - r'_i|)^{-1} - \sum Z_n e^2 (|R_n - r'_i|)^{-1} + \frac{1}{2} \sum Z_n Z'_n e^2 (|R_n - R'_n|)^{-1}, \quad (11)$$

where n is atomic nuclei numbers ($n = 1, \dots, N_n$); i is electron numbers ($i = 1, \dots, N_e$); N_n, N_e is the number of atomic nuclei and electrons, respectively, in the system; R, P are position and momentum of the nucleus; r, p are position and momentum of the electron; M and m are the mass of the nucleus and the mass of the electron; Z is the atomic number of the nucleus; e is the electron charge.

The Schrödinger equation with wave function $\Psi(R_1, \dots, R_{N_n}, r_1, \dots, r_{N_e})$ for system (11) will be written as:

$$H\Psi(R_1, \dots, R_{N_n}, r_1, \dots, r_{N_e}) = E\Psi(R_1, \dots, R_{N_n}, r_1, \dots, r_{N_e}),$$

$$\int \Psi(R_1, \dots, R_{N_n}, r_1, \dots, r_{N_e}) \times \Psi^*(R_1, \dots, R_{N_n}, r_1, \dots, r_{N_e}) dR_1 \dots dR_{N_n} dr_1 \dots dr_{N_e} = 1. \quad (12)$$

However, the Schrödinger system of equations cannot be solved practically, since the function sought here is the function $3(N_n + N_e)$ of real variables (N_n, N_e are the number of atomic nuclei and electrons in the system, respectively). If you select only 10 nodes for each considered variable, then the difference equations will contain $10^{N_n + N_e}$ of the unknowns. For the object of modeling with only 10 atoms (which is very small), taking into account the number of electrons present, the number of unknowns will be a very large number. Reducing the dimension of the problem is possible only by taking into account its features. This circumstance does not allow using the considered approach for modeling processes in arc discharge plasma, where a huge number of various particles are simultaneously moving and interacting.

The above analysis of the methods shows that for modeling arc discharge processes of motion and interaction of different particles in multicomponent plasma, taking into account their collisions, the quantum-kinetic approach based on the Boltzmann kinetic equation supplemented by the system of Maxwell equations for description of a self-consistent electromagnetic field is most suitable. The use of the distribution functions of various plasma components makes it possible to predict the behavior of carbon particles in the synthesis process by considering collective plasma phenomena – plasma oscillations, fluctuations of various characteristics, concentrations and particle fluxes – on the basis of a probabilistic approach.

The development of a mathematical model of the plasma synthesis processes of the CNSs based on the Boltzmann kinetic equation (7) implies the use of significant computational resources for the numerical solution of the problems posed, but the use of modern methods and algorithms for the organization of parallel and distributed calculations allows solving this problem.

Mechanism of the CNS formation in low-temperature plasma

When developing a mathematical model of plasma processes for the CNS synthesis, it is necessary to take into account the adopted mechanism of interaction of elements in plasma and features of the system under consideration. The mechanism of the CNS formation in arc discharge plasma is still not clearly defined. There is a theory of the formation of carbon nanotubes constructed on the basis of the mechanism of the longitudinal sequential extension of a nanotube with carbon ions. In the process of synthesis, a nanotube fragment appears on the cathode surface, at the end of which the electric field is larger. As a result, carbon ions begin to attract at its end, and not at its side surface, which causes the growth of the nanotube in the direction of the electric field [14].

However, the use of catalysts drastically changes the described picture of the CNS formation, which cannot be explained by this theory. Also, such a theory does not explain the formation of fullerenes in plasma without deposition on the cathode.

The introduction of a catalyst into graphite electrodes stimulates the growth of single-walled carbon nanotubes (SWCNT). Without participation of the catalyst, predominantly multi-walled carbon nanotubes (MWCNTs) are formed, growing perpendicularly to the flat surface of the cathode end. The mechanism of the catalytic effect of metals on the

formation of single-walled carbon nanotubes is similarly described in the literature [15] and consists of the adsorption of carbon atoms on the surface of metal particles and their free movement to the base of the growing nanotube. It was hypothesized why the use of a catalyst does not form MWCNTs. This process is possible only under a combination of conditions related to the coordinated interaction of a large number of particles. The formation of small diameter SWCNTs with the use of metal catalysts is explained by the fact that nanotube growth occurs on the surface protrusions of metal particles whose diameter is small compared with their height. In comparison with simple catalysts, the use of mixed catalysts (Ni/Co (Fe), Ni/Y (Ca, Ce) and Rh/Pt (Pd), etc.) gives greater efficiency. This is due to a change in the activation energy of nanotube growth, increased carbon adsorption, and the formation of a surface that has more protrusions.

However, the theory considered above cannot answer all the features and factors of the processes of plasma synthesis under different conditions and therefore cannot be generally accepted.

The above analysis of various mechanisms of the CNS formation in plasma showed the promise of using the following scheme for electric arc synthesis:

- Under the influence of high temperature in plasma, the layered structure of a graphite anode is destroyed and sublimation occurs (at a temperature of > 4200 K) of carbon ions from the anode, which is bombarded by a stream of electrons;
- Electromagnetic field provides accelerated movement in plasma of carbon ion flux from the anode to the cathode;
- In the process of movement, carbon ions collide with inert gas ions and electrons, as well as between themselves;
- When carbon ions collide between them under certain spatial-energetic conditions, a stable covalent bond can be formed leading to the formation and growth of the C_2 and C_3 cluster groups;
- C_2 and C_3 cluster groups form more complex structures in the plasma – fullerenes, and when interacting with the cathode – nanotubes.

The basis of such a mechanism for the formation of stable cluster carbon groups in plasma is an approach consisting in the formation of energy bonds between carbon ions during elastic impact, when particles approach a distance shorter than the covalent bond length with a total energy greater than the activation energy of a chemical bond.

The above-described mechanism for the formation of various carbon cluster groups that form bulk CNSs in plasma arc discharge is shown in Fig. 3.

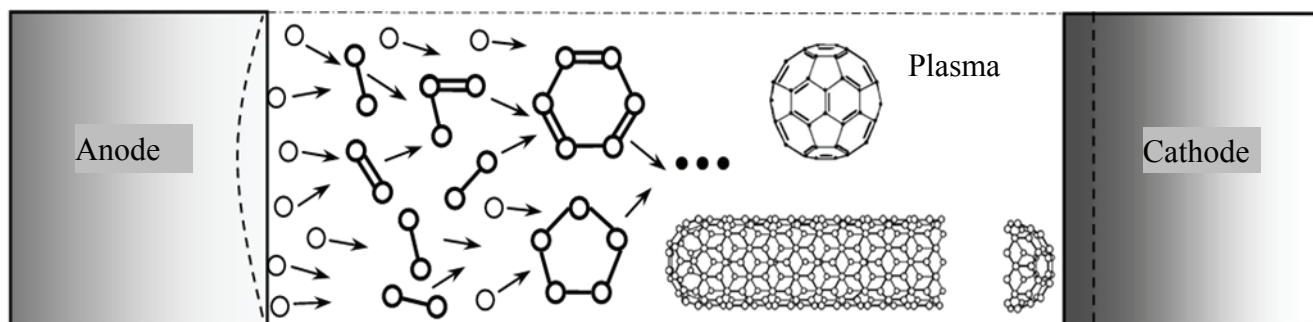


Fig. 3. Mechanism of CNS formation in arc discharge plasma

To simplify the construction of a mathematical model of the motion and interaction of particles in an arc discharge plasma, the influence of the catalyst will not be taken into account. At the initial stage of modeling the synthesis of CNSs in plasma, the influence of the catalyst on the formation of the C_2 and C_3 cluster groups is insignificant, due to the small evaporation region and the number of particles compared to graphite raw materials. The greatest influence of catalyst particles on the process of the CNS formation occurs at the cathode, when carbon cluster groups become commensurate with the mass of catalyst.

The use of metal catalysts under the same synthesis conditions leads to a decrease in the synthesis temperature, a decrease in the energy of the interacting particles and a change in the pattern of interactions in plasma.

Building a model of the motion and interaction of particles in plasma using the quantum-kinetic approach

Based on the analysis of the modeling approaches to building a mathematical model of the processes of motion and interaction of various particles in arc discharge plasma during the CNS synthesis, the quantum-kinetic approach based on the use of the Boltzmann kinetic equation is the most expedient. This method operates with the distribution functions of charged (probability density) particles on coordinates and velocities, which allows consideration of collective phenomena in plasma with a high degree of probability to predict the characteristics and variety of processes in the system under consideration, as well as reduce the computational complexity of the developed model.

When building a mathematical model of the complex system under consideration, we make the following assumptions:

1) arc discharge plasma is low-temperature, non-equilibrium;

2) plasma consists of electrons, singly charged carbon cations, buffer gas, and carbon clusters;

3) the CNS synthesis occurs without catalysts;

4) particle interactions in a multicomponent plasma are considered on the basis of pair elastic and inelastic collisions;

5) the formation of carbon clusters occurs by ion-molecular synthesis;

6) the condition for the occurrence of a stable bond is the convergence of particles a distance less than the length of the covalent bond with the total kinetic energy greater than the activation energy of the chemical bond E_{bond} ;

7) carbon cations form only aggregates C_2 and C_3 ;

8) depending on the particle energy E_{part} , bombarding the cathode, the process of its reflection or deposition occurs ($E_{\text{part}} < E_{\text{bond}}$ – particle reflection, $E_{\text{part}} > E_{\text{bond}}$ – particle deposition);

9) the ratio of the energies of the particles bombarding the cathode:

$$E_{\text{refl}} < E_{\text{bond}} < E_{\text{depos}} < E_{\text{sput}} < E_{\text{impl}},$$

$$E_{\text{sput}} = \frac{(1 + m_1/m_2)^2}{m_1/m_2} E_{\text{subl}},$$

where energies: E_{refl} is reflection; E_{depos} is deposition; E_{sput} is sputtering (atom sputtering); E_{impl} is implantation; E_{subl} is sublimation; m_1 , m_2 are masses of particles sputtered and bombarding the surface.

The system of Boltzmann kinetic equations (7) written with allowance for the designated features of the process under consideration will take the form:

$$\frac{\partial f_\alpha}{\partial t} + \vec{\nabla} \frac{\partial f_\alpha}{\partial \vec{r}} - \frac{q_\alpha}{m_\alpha} \left(\vec{E} + \frac{1}{c} [\vec{\nabla}, \vec{B}] \right) \frac{\partial f_\alpha}{\partial \vec{\nabla}} = \frac{\partial f_\alpha}{\partial t} \Big|_{\text{coll}},$$

$$\alpha = e, c, h, \quad (13)$$

where f_α is plasma component distribution functions; $\alpha = e, c, h$ is particle type (e is electron, c is carbon, h is helium); q_α, m_α are particle charge and particle mass, respectively.

The collision operator (8) will be the sum of the integrals of pair collisions between particles in the form:

$$\left. \frac{\partial f_\alpha}{\partial t} \right|_{\text{coll}} = \sum_{k=e,c,h} \iint_V (f'_\alpha f'_k - f_\alpha f_k) |\vec{\mathfrak{g}} - \vec{\mathfrak{g}}'| d\sigma d\vec{\mathfrak{g}}', \quad (14)$$

where V is the volume of the calculated plasma region. In the collision integral (14), all plasma components interacting with each other are taken into account.

We use the Maxwell distribution [16] as a function describing the velocity distribution of particles in arc discharge plasma.

To find the parameters of the electromagnetic field, the original system of equations (13) – (14) must be supplemented with the system of Maxwell equations and the equations that determine the dependences of the current density $\vec{j}$ and charge ρ through the velocity distribution functions of particles:

$$\begin{cases} \text{rot} \vec{H} = \frac{4\pi \vec{j}}{C} + \frac{1}{C} \frac{\partial \vec{D}}{\partial t}, \\ \text{rot} \vec{E} = -\frac{1}{C} \frac{\partial \vec{B}}{\partial t}, \\ \text{div} \vec{B} = 0, \\ \text{div} \vec{D} = 4\pi \rho, \\ \rho = \frac{q_e}{m_e} \int_V (f_c + f_h - f_e) d\vec{\mathfrak{g}}, \\ \vec{j} = \frac{q_e}{m_e} \int_V (f_c + f_h - f_e) \vec{\mathfrak{g}} d\vec{\mathfrak{g}}. \end{cases} \quad (15)$$

Here $\vec{D}$ is electric induction.

Initial conditions at $t = 0$:

$$\begin{aligned} f_\alpha(\vec{r}, \vec{\mathfrak{g}}, 0) &= f_\alpha^0, \quad \alpha = e, c, h, \\ E(\vec{r}, 0) &= E^0, B(\vec{r}, 0) = B^0. \end{aligned} \quad (16)$$

Boundary conditions at the anode (A):

$$\begin{aligned} \vec{r} \in |_A: f_e(\vec{r}, \vec{\mathfrak{g}}, t) \Big|_{\vec{r} \in |_A} &= f_e^0, \\ f_c(\vec{r}, \vec{\mathfrak{g}}, t) \Big|_{\vec{r} \in |_A} &= f_c^0, \\ f_h(\vec{r}, \vec{\mathfrak{g}}, t) \Big|_{\vec{r} \in |_A} &= f_h^0, \\ f_\alpha^0 &= f_\alpha^{\text{maksv}}. \end{aligned} \quad (17)$$

The resulting system of nonlinear differential equations (13) – (15) with initial (16) and boundary conditions (17) is a mathematical model that describes the motion and interaction of particles in multicomponent plasma, using the probabilistic approach, and allows predicting the diversity of the processes occurring in the plasma for the given synthesis. The solution of this system of equations determines the density distribution functions of particles in plasma – f_e, f_c, f_h .

The presence of the vector equation (13) of the collision integral (14) in the right-hand side causes considerable difficulties in solving the equations of the model. The representation of the collision integral in the form of the Fokker-Planck equation allows going over to the equations taking into account the increments of the velocity components, and then from vector algebra at each point in space to tensor analysis [17]. By performing the necessary intermediate transformations, the system of equations (13) is reduced to a dimensionless form in the three-dimensional coordinate system:

$$\begin{aligned} \frac{\hat{f}_\alpha}{\hat{\partial t}} + \sqrt{\delta_\alpha} \left\{ \hat{\mathfrak{g}}_r \frac{\partial \hat{f}_\alpha}{\partial \hat{r}} + \frac{Z_\alpha}{2\epsilon_\alpha} \hat{E}_r \frac{\partial \hat{f}_\alpha}{\partial \hat{\mathfrak{g}}_r} \right\} = \\ = K_\alpha \left\{ \frac{1}{2} G_\alpha \frac{\partial^2 \hat{f}_\alpha}{\partial \hat{\mathfrak{g}}^2_r} + C_\alpha \frac{\partial \hat{f}_\alpha}{\partial \hat{\mathfrak{g}}_r} + R_\alpha \right\}, \end{aligned} \quad (18)$$

where $K_\alpha, G_\alpha, C_\alpha, R_\alpha$ are coefficient matrices with a size of (3×1) ; Z_α is electron charge ratio; $\delta_\alpha, \epsilon_\alpha$ are proportionality coefficients.

To find a solution, the resulting system of equations (18) using the splitting method is divided into two auxiliary problems, which are solved sequentially [18]:

$$\frac{\hat{f}_\alpha}{\hat{\partial t}} = \tilde{Q}_1 \hat{f}_\alpha + \tilde{Q}_2 \hat{f}_\alpha, \quad (19)$$

where

$$\tilde{Q}_1 \hat{f}_\alpha = -\sqrt{\delta_\alpha} \left\{ \hat{\mathfrak{g}}_r \frac{\partial \hat{f}_\alpha}{\partial \hat{r}} + \frac{Z_\alpha}{2\epsilon_\alpha} \hat{E}_r \frac{\partial \hat{f}_\alpha}{\partial \hat{\mathfrak{g}}_r} \right\}, \quad (20)$$

$$\tilde{Q}_2 \hat{f}_\alpha = K_\alpha \left\{ \frac{1}{2} G_\alpha \frac{\partial^2 \hat{f}_\alpha}{\partial \hat{\mathfrak{g}}^2_r} + \tilde{C}_\alpha \frac{\partial \hat{f}_\alpha}{\partial \hat{\mathfrak{g}}_r} + \tilde{R}_\alpha \right\}. \quad (21)$$

The first problem (20) is a system of dimensionless Vlasov-Poisson equations describing the transfer of particles, and the second task (21) defines pair collisions of charged particles in plasma.

Solving problem (20) allows finding an intermediate function that determines the initial

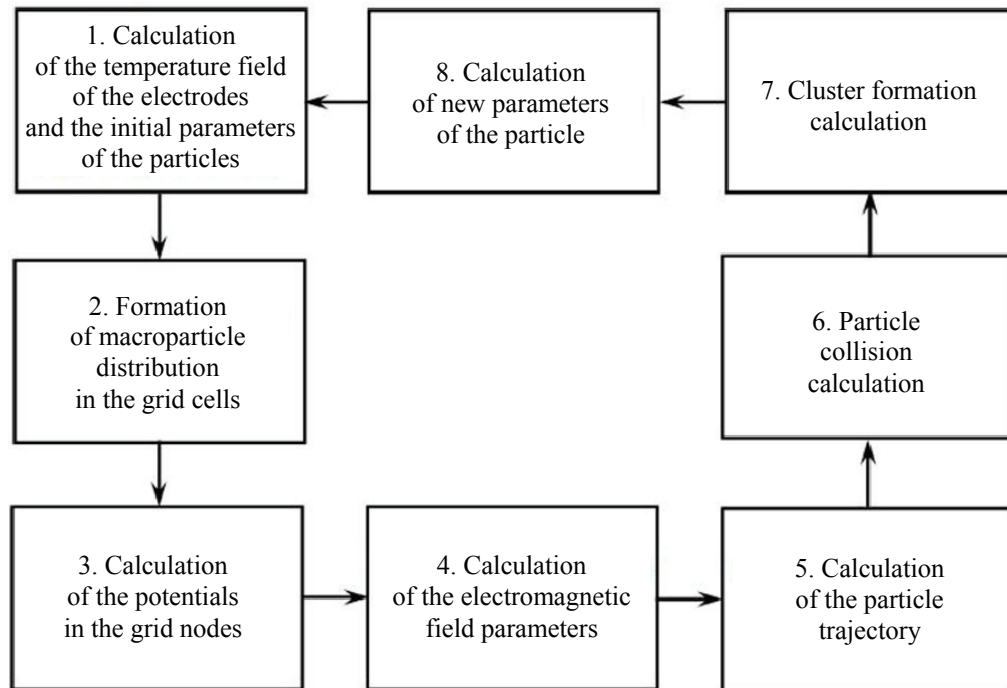


Fig. 4. Procedure for the model solution

condition for finding the numerical solution of the second problem.

As a result of solving the second problem (21), which takes into account particle collisions, the coefficients are found in the collision integrals; this makes it possible to obtain particle distribution functions for the considered time points Δt .

To construct a numerical solution of the system of equations (18), it is necessary to specify the initial velocities of carbon particles during the destruction of the anode and electrons from the cathode. It is possible to do this knowing the temperature field distribution at the anode-plasma and cathode-plasma borders [19].

As previously noted, modelling of plasma processes is a very resource-intensive task associated with the processing of large amounts of data due to the simultaneous presence in the phase space of a huge number of heterogeneous particles. Therefore, to reduce the volume and computation time required for numerical solution of the problems of the constructed model, it is advisable to use the large particles method (LPM) to reduce the number of particles of the same type in the calculation by grouping them to a reasonable level into larger particulates without loss of calculation accuracy [20].

The procedure for the numerical solution of the problems of the constructed mathematical model based on the use of the quantum-kinetic approach using the LPM is shown in Fig. 4.

The procedure for the solution includes the sequential execution of eight basic steps of the model. It is possible to reduce the total time to solve these problems by the organization of distributed parallel computing on the CPU and GPU. The use of parallelization technology on CPUs and GPUs makes it possible to use high-performance PC graphics cards for general-purpose computing, which greatly increases the efficiency of processing large amounts of data without using supercomputers or large computing clusters [21].

Results and discussion

To determine the conformity of the constructed mathematical model on the basis of the Boltzmann kinetic equation to the physical process of arc synthesis of a CNS, a series of field experiments were carried out at the CNS synthesis by using the electric arc method. The results of the studies performed on the cathode deposit growth rate on the arc current are presented in Fig. 5.

The calculated growth rate of deposit sediment at the cathode was determined using the distribution function of carbon ions in the cathode region based on the expression:

$$\vartheta_d(t) = m_c \int \int_{WD} f_c dr d\vartheta. \quad (22)$$

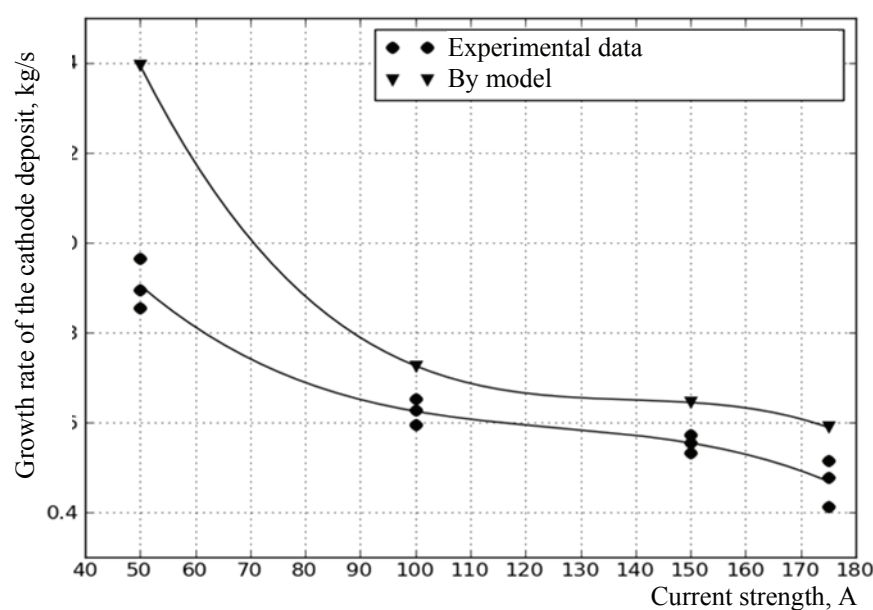


Fig. 5. Change in the growth rate of cathode sediment from the current strength

The values of the arc current represented on the abscissa axis are obtained from the current density using the formula:

$$I(t) = \int_S \vec{j} dS, \quad (23)$$

where m_C is carbon ion mass; W is the velocity region of carbon particles, which satisfy the conditions of deposition on the cathode surface or reflection,

depending on the kinetic energy of the particle; D is calculated area of the cathode region; S is the arc cross section.

The synthesis parameters for field and numerical calculations were set: the diameter of graphite electrodes was 0.012 m, the interelectrode distance was 0.01 m, the voltage between the electrodes is 25 V, the helium pressure in the synthesis chamber was 53.3 kPa.

The relative error of the calculated value of the growth rate of the cathode sediment obtained by the model in comparison with the experimental data, with an arc current strength of 150 A was $\delta \approx 16,3 \%$.

The use of the velocity distribution functions of carbon particles calculated by the model makes it possible to investigate the zones and conditions for the likely formation of the highest concentrations of linear cluster in the plasma. An example of the calculations performed on the model of the change in the number of interactions and the formation of cluster groups C—C and C=C—C in plasma along the length of the interelectrode space is presented in Fig. 6 and Fig. 7

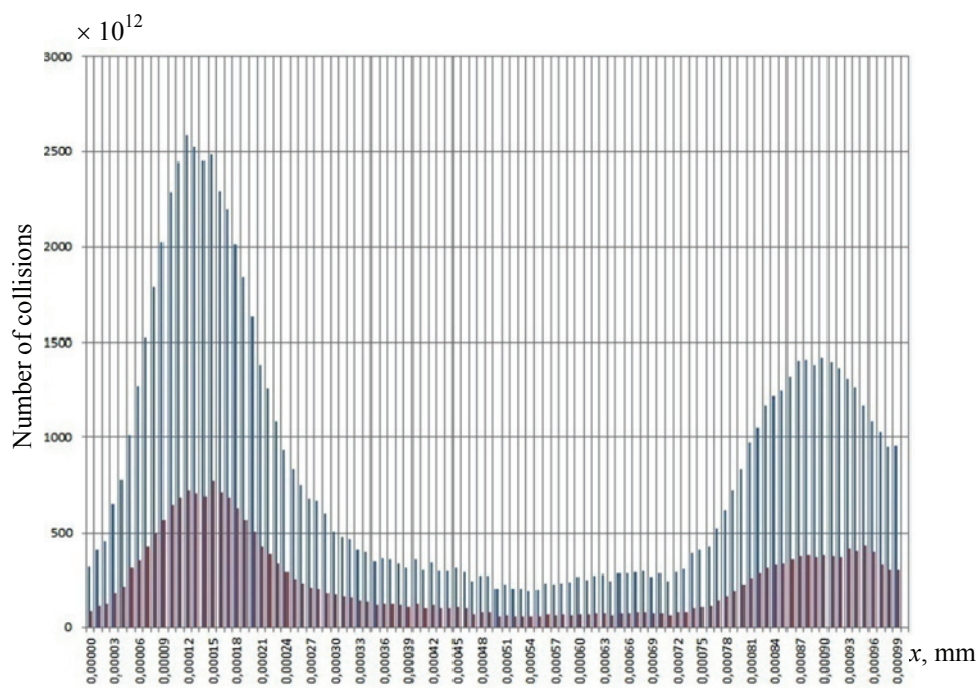


Fig. 6. Dependence of the number of collisions and the formation of cluster groups C=C along the length of the interelectrode space
 ■ – total number of interactions; ■ – number of interactions with the formation of C=C bond

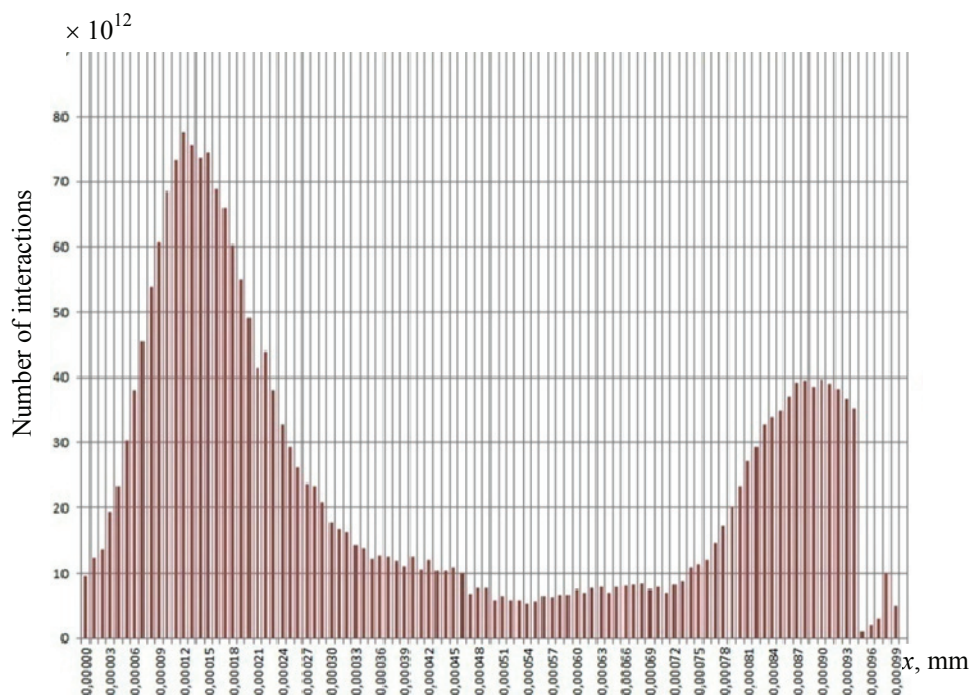


Fig. 7. The number of formations of cluster groups $C=C-C$ along the length of the interelectrode space
 ■ – number of interactions with the formation of $C-C=C$ bond

Presented in Fig. 6 and Fig. 7 numerical calculations are performed for the time interval $\Delta t = 360$ ns.

The study of the results of mathematical modeling showed that the formation of cluster groups is most influenced by the number of collisions. The ratio of the number of collisions with the formation of bonds to the total number of collisions under the conditions studied does not change significantly. The total number of collisions is determined by the concentration of particles, their speed and size.

When moving in plasma, particles increase in size due to the formation of bonds in collisions with other particles, accelerate under the influence of an electric field, but the total number of particles decreases. At the initial stage, there is the largest number of particles with a relatively low speed. And a large number of particles give a large number of collisions, some of which lead to the formation of bonds and the enlargement of particles. The number of particles decreases, the concentration of particles decreases, which leads to a decrease in the total number of collisions and collisions with the formation of bonds. Further, already larger particles are accelerated by the electromagnetic field, which leads to an increase in the total number of collisions in the cathode region, and consequently, in the number of bonds formed.

Conclusion

In this paper, two main tasks were set: first, to perform an analysis of existing approaches to the modeling of processes in plasma as applied to plasma synthesis of carbon nanostructures; secondly, to develop a mathematical model of the synthesis of CNS processes in arc discharge plasma.

The analysis of the approaches to modeling plasma synthesis processes has confirmed that the quantum-kinetic approach allows one to describe the motion and collisions of particles in a multicomponent low-temperature plasma in a large range of linear dimensions of nanostructures. Using the distribution functions of various plasma components on the basis of the probabilistic approach makes it possible to consider collective phenomena in plasma. The use of the indicated approach assumes significant computational costs for numerical solution of the model's problems; however, the use of modern methods and algorithms for the organization of computations allows solving this problem.

The analysis of the approaches to modeling plasma synthesis processes has shown the promise of a quantum-kinetic approach that allows one to describe the motion and collisions of particles in a multicomponent low-temperature plasma in a large range of linear dimensions of nanostructures. Using

the distribution functions of various plasma components on the basis of the probabilistic approach makes it possible to consider collective phenomena in plasma. The use of the indicated approach assumes significant computational costs for numerical solution of the model's problems, but the use of modern methods and algorithms for the organization of computations allows solving this problem.

The mechanism of the formation of CNS in the plasma of the arc discharge is considered, taking into account the formation and growth of cluster groups of carbon. Based on the quantum-kinetic approach, using the Boltzmann kinetic equation, a mathematical model of the CNS synthesis process was developed, which allows describing the formation of linear cluster carbon groups, which are the basis of bulk nanostructures, in a low-temperature plasma. The difficulties that arise in the numerical solution of the problems of the model are indicated, and methods for overcoming them are proposed. The results of the correspondence of the developed model to the physical process of the CNS synthesis are presented.

A study of the numerical characteristics of collisions and the formation of cluster groups C_2 and C_3 along the length of the interelectrode space showed the heterogeneity of the process of their formation in the plasma. The number of collisions and the cluster group formation depends on the concentration velocity and particle size.

The developed model allows us to investigate the characteristics and properties of the processes of formation, various CNSs in plasma, taking into account the characteristics of the synthesis. In this paper, the authors did not pose the problem of modeling the CNS synthesis, taking into account the catalyst of the additional complexity of solving the problem. When making the necessary changes, the developed full model will make it possible to perform numerical calculations of the CNS synthesis processes in a low-temperature plasma with a catalyst at the anode.

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