PHYSICS OF CLUSTERS

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Preface

This monograph is devoted to a relatively new but an extremely fast developing field of cluster physics. The experimental investigations of clusters started since the molecular beam technique was developed and clusters were produced. At present there are many ways to produce clusters. Modern methods allow one to separate clusters containing a fixed number of atoms or molecules and which have a certain structure. From the point of view of fundamental physics, the clusters are perfectly isolated finite-dimensional systems. Here, we only outline the potentialities and applicability of clusters. The clusters being isolated and finite objects are most suitable to apply methods of classical and quantum molecular dynamics. On the other hand, physics of clusters is a new field of research, since it overcomes the gap between physics of atoms and condensed matter theory. Clusters are used in a wide region of applications. Being very active chemical catalyzers, they are used to purify oil. The possibility to create three-dimensional periodical structures from clusters opens new directions in chemistry and nanotechnology. The formation of films from clusters with required properties also creates new perspectives in microelectronics. Lasers and other new types of sources of light such as clusters lamps can be produced on the basis of clusters. The possibility of application of clusters in nuclear synthesis is also discussed.

The monograph is based on talks given at the Cluster Workshops, which were held in Pushchino in 1995 and 1996. It includes reviews, reports devoted to new methods, numerical modeling, and special topics. The reports focus not only on the fundamental physical properties of clusters such as their geometric and electronic structure, as well as on optical, thermal and magnetic properties, but also on a broad spectrum of their potential applications. These include nucleation and growth of small particles, fabrication of new materials with predefined properties (cluster-assembled and nanostructures). Some aspects of simulations and calculations of small particles and clusters are also discussed. We hope our monograph will be of interest to a broad range of readers who will be able to sense the excitement of the talks.

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FORMATION OF FULLERENES, ONIONS AND OTHER NANOMETER SIZE CARBON CLUSTERS

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Various models for the formation of fullerenes and other carbon nanostructures – nanoparticles ("onions"), nanotubes and cones are analyzed. Consideration is given to the following models of fullerene formation: assembling from graphite sheets, assembling of microclusters, models of "nautilus" and "fullerene road" and different ways of annealing from clusters with other structure. The selection of abundant fullerenes and their isomers as a result of annealing of carbon clusters and subsequent insertion and emission of molecule C_2 by fullerenes are discussed. The mechanisms of carbon nanoparticle formation and their relation to the models of fullerene formation are studied. Molecular dynamic simulation of possible mechanisms of nanoparticle formation is reviewed. Possible nuclei for the growth and growth mechanisms of single-shell and many-shell nanotubes and cones are discussed. Possible methods for the formation of carbon nanostructures based on the mechanisms considered are described: (a) a method for the creation of great abundant fullerenes; (b) a method for obtaining carbon nanoparticles with a metal core consisting of tens atoms; (c) fabrication of a crystal from single-shell nanotubes of the same diameter.

1 Introduction

The experimental detection of a stable cluster C_{60} with icosahedral symmetry [1] and a large variety of other fullerenes in succeeding years can be ranked among the most brilliant discoveries of the last decade. Curl, Kroto, and Smalley were awarded the Nobel prize for this outstanding finding. The surprising thing is that the new carbon state was found after the long-standing use of various forms of this substance and the comprehensive study of well-known graphite and diamond. Curiously, quantum chemical calculations predicted the existence of C_{60} well before. [2] We will not discuss here the history of C_{60} discovery and concentrate on the question of what is the mechanism for the formation of this complicated and symmetrical cluster in real experimental conditions. It can be alternatively reformulated with emphasis on more applied aspects of the problem. Let us assume that according to calculations a complicated cluster (or complicated molecule) may exist. What is a possible mechanism for its formation? What are the best conditions for its production? The adequacy of raising these questions is by no means apparent if we refer them to complicated biological molecules like nucleic acids. Or in other words, what

is the limit of *molecular design*? These questions are particularly acute nowadays in connection with the possibility of producing various cluster materials and nanostructures. In this review we have restricted ourselves to the discussion of possible mechanisms for the formation of fullerenes and other carbon nanostructures such as nanoparticles, nanotubes, and cones.

By now several reviews were devoted to formation of fullerenes,[3–5] nanoparticles,[4] and nanotubes.[6,7] However a variety of carbon nanostructures have not been considered in a one review. Moreover a commonly accepted schemes for the formation of a carbon nanostructures are still lacking and the models discussed are only hypothetical. Therefore new experimental and theoretical data accumulated in this actual quickly developing field need systematization and critical comprehension.

2 Models of fullerene formation

2.1 Formation and structure of fullerenes

Fullerenes were discovered due to the interpretation of the following experimental fact: in a mass spectrum measured under certain ablation conditions the peak corresponding to C_{60} was 40-fold higher than the peaks corresponding to other clusters.[1] To explain this phenomenon, the authors of[1] assumed the existence of a stable cluster C_{60} in the form of a truncated icosahedron in which all atoms lay on a sphere in the vertices of 12 regular pentagons and 20 hexagons. This cluster was referred to as fullerene. Apart from the fullerene experiments revealed some other carbon clusters with similar structure which consisted of tens or hundreds of atoms lying on a spheroidal surface in the vertices of pentagons and hexagons. One of the main criteria for the adequacy of a model for the fullerene formation is its capacity to explain greater abundance of fullerene C_{60} relative to other fullerenes. An important breakthrough was the production of fullerene C_{60} in macroscopic amounts by ablation of graphite electrodes in arc discharge.[8] Subsequently, some other methods of fullerenes production were proposed and a number of experiments were carried out to investigate conditions and processes of fullerenes formation. As new experimental facts were revealed, new models of fullerene formation were proposed to explain them. However, the question is still to be clarified. In this section we analyze the models for fullerene formation dealing mainly with the assembling of fullerenes in carbon plasma and leaving aside alternative possibilities for their formation (such as reactions between hydrocarbons, for example).

The classification scheme for carbon plasma conditions where fullerenes form were suggested.[9] This classification is based on the type of stream deter-

nined the rate of carbon plasma expansion. The plasma expansion is described by equation

$$\frac{n_c(r)}{u(r)} = \frac{n_c(r_0)}{u(r_0)} \left(\frac{r}{r_0}\right)^{-\eta}, \qquad (1)$$

where n_c is a local density of carbon, u is a local velocity of carbon plasma or buffer gas containing plasma, η is a parameter depending on type of stream.

1. $\eta = 0$ corresponds to turbulent stream. This type of stream take place in arc discharge reactor filled with buffer gas.

2. $\eta = 1$ corresponds to turbulent flame.

3. $\eta = 2$ is a case of "spherical" expansion. This type of stream occurs in a supersonic beam and in an arc discharge reactor in the absence of buffer gas.

4. $\eta = 3$ is a case of "explosive" expansion corresponding to first stage of laser ablation.

It was proposed in the review [5] that mechanisms of fullerene formation may be different at conditions of laser ablation and in arc discharge reactor filled with buffer gas. Here we discuss the models of fullerene formation in relation with conditions in carbon plasma.

2.2 Fullerene assembling from graphite sheets

Fullerene C_{60} was initially assumed to assemble from plane sheets evaporated from graphite. [10] The simplest assembling is joining of six clusters C_{10} consisting of twin hexagons. [11,12] Another possibility is rolling of graphite sheets into caps making up halves of fullerene [11,12,13] C_{60} (Fig. 1) which subsequently join with smaller graphite fragments to form fullerene [11,12] C_{60}. According to this beautiful model, the formation of fullerene C_{60} is optimal and have a large yield when these fragments are the main products of graphite ablation. However, the model fails to explain the following facts.

1. Soot obtained as a result of graphite ablation under optimal conditions contains [14] up to 13% of C_{60}. Hence according to the model, a significant part of evaporated graphite must be sheets of a special shape which seems unlikely.

2. Fullerene C_{60} is formed not only as a result of graphite evaporation but also upon ablation of other materials which evaporate as clusters of various shape. Among these are polymers (see, for example, [15–19]) higher carbon oxides, [20,21] and soot produced upon benzene combustion. [22] Fullerene C_{60} is synthesized in a reactor filled with a mixture of C_2H_2 and He (Ref.[23]), as well as a mixture of C_2H_2 and SF_6 (Ref.[24,25]), fullerenes also arise in flame. [26,27]

3. The mass spectra of fullerenes enriched by isotope ^{13}C which were studied in [28] cannot be explained by the fullerene assembling from graphite sheets.

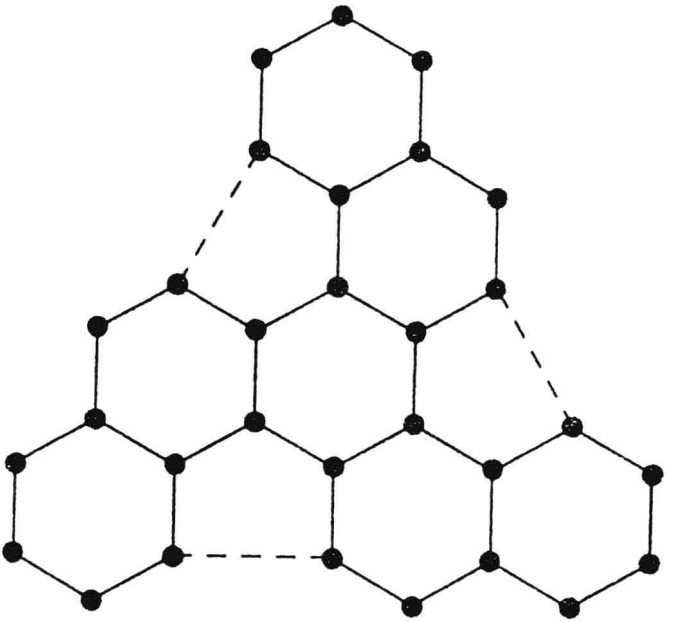

Figure 1: The plane sheet curved into the cup which makes up a half of fullerene C_{60}.[12] The bonds formed during the process are shown by the dashed lines.

Fullerenes in that experiment were produced under the conditions optimal for the synthesis in arc discharge between graphite electrodes. In graphite containing 98.9 % of ^{12}C holes were made, which were filled with amorphous ^{13}C. If the main channel for the formation of fullerene C_{60} is the assembly of graphite sheets consisting of tens of atoms, the mass spectrum must reveal fullerenes formed from the graphite carbon alone and, hence, consisting mainly of ^{12}C. However, the mass spectrum observed in the experiment indicated that carbon atoms mixed completely in plasma before precursor clusters arose.

2.3 "Nautilus" model

Another model for the fullerene formation will be referred to, for brevity, as the "nautilus" model.[29–33] According to the model, a carbon cluster growing in plasma during fullerene synthesis looks like a curved sheet, where carbon bonds are arranged in pentagons and hexagons, as in the fullerene structure. While growing the sheet rolls itself so that to minimize the number of free bonds.

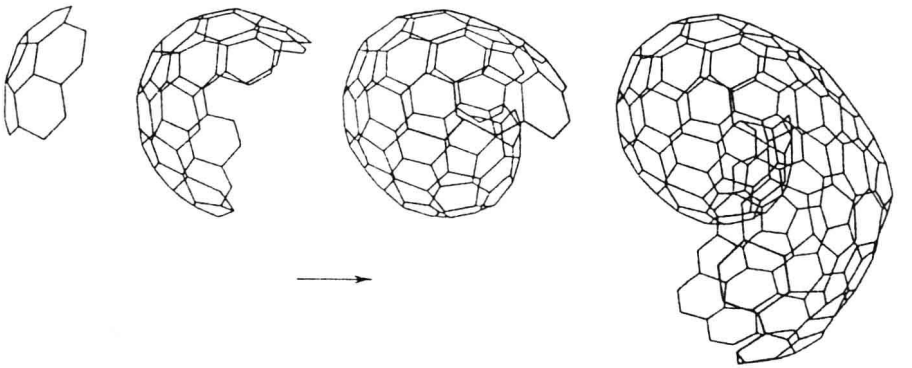

Figure 2: The growth of a carbon cluster according to the nautilus mode.[31]

The growth of the carbon cluster is similar to that of nautilus (Fig. 2). Some growing clusters can close accidentally into fullerenes. Others grow further forming "quasispiral" soot particles. Contrary to the model discussed above this model does not relate the fullerene formation to graphite evaporation, but it cannot explain the high yield of fullerene C_{60} under certain conditions of synthesis (see, for example, [14,34]). Moreover, the studies of the second ionization potential and thermal ion emission of great carbon clusters up to C_{300}, forming together with C_{60}, reveal them to be fullerenes rather than quasispiral particles. [35] It was proposed in [14] that soot in flame is also formed according to the "nautilus" model. However, there is evidence contradictory to this hypotheses: (a) chemical properties of the soot particles are closer to those of benzene than to those of graphite; [36,37] (b) The X-ray scattering spectrum of soot particles is more similar to that of polycyclic aromatic hydrocarbons than to that of graphite. [37]

2.4 Assembling from microclusters

In this section we analyze the models, according to which fullerenes assemble from various clusters whose structure coincides with that of fullerene fragments. The drawback of the above models are corrected by the "pentagon road" rule. [38,39] According to this model, a growing carbon sheet anneals so that the pentagons are maximally separated by hexagons producing, eventually, fullerene C_{60}. The overwhelming majority of carbon clusters larger than C_{30} contain only even numbers of atoms (see, for example, [1,18,40] therefore the

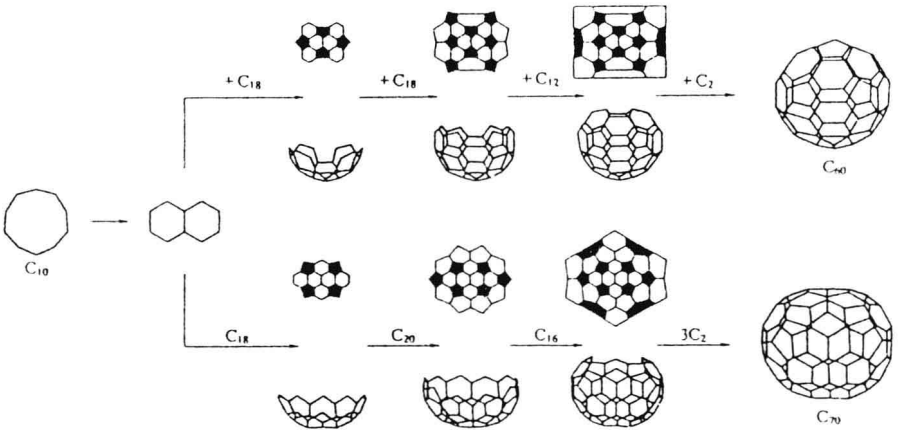

Figure 3: The assembling of fullerene C_{60} according to the ring stacking model.[44]

"pentagon road" was improved by the assumption that the growth of C_{60} occurs with successive addition of C_2.[41] Some schemes of C_{60} and C_{70} formation according to the improved pentagon road are given in [42]. There are several models for the assembly of fullerenes from large precursors, namely, C_{60} from two C_{30}, [13] from three C_{20}, [42] C_{60} from six C_{10}, [11,12,43] "ring stacking" model (Fig. 3): $C_{10}+C_{12}+2C_{18}+C_2=C_{60}$, [44,45] $2C_{10}+2C_{20}+C_{24}=C_{84}$, [46] $C_{10}+C_{18}+C_{20}+C_{16}+3C_2=C_{70}$, [45] and a number of ways of stacking from other similar precursors.[47]

The authors of "ring stacking" model [44-46] believed that the model could be verified by the NMR detection of isomer C_{84} with a certain symmetry.[48] But a more recent NMR study of C_{84} [49] did not reveal this isomer among C_{84} isomers.

The above models of fullerene formation, [38,39], [41-47] imply the existence of certain precursors of C_n whose structure is similar to that of fullerene fragments. Such precursors are assumed to be polycyclic plane sheets at $n = 10 - 19$, and curved polycyclic cap-like sheets involving only pentagons and hexagons at $n > 20$. On adding hydrogen in a buffer gas during fullerene synthesis (to interrupt it) polycyclic aromatic hydrocarbons C_nH_m with $n = 15 - 20$ were obtained [42] whose structure was similar to that of the model fullerene precursors.[38,39,41-47] But this fact does not prove that hot carbon clusters which formed the hydrocarbons on plasma cooling had the same sizes and structure. To the contrary, both the theoretical calculations of the energy of various carbon clusters, [50-53] and the experimental study of the cluster mo-