Exotic objects of atomic physics

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Abstract There has been presented a short survey of physical properties, methods of production and exploration as well as directions of practical usage of the objects of atomic physics which are not yet described in detail in modern textbooks and manuals intended for students of technical universities. The family of these objects includes negative and multi-charged ions, Rydberg atoms, excimer molecules, clusters. Besides of that, in recent decades this family was supplemented with new nanocarbon structures such as fullerenes, carbon nanotubes and graphene. The textbook “Exotic objects of atomic physics” [1] edited recently contains some information on the above-listed objects of the atomic physics. This textbook can be considered as a supplement to classic courses of atomic physics teaching in technical universities.

1. Introduction

The atomic physics was created initially as a science exploring properties of tiny atomic particles such as atoms, ions and electrons. As the science was developed this family of particles was supplemented with new objects such as molecules and molecular ions. Properties of all these objects are studied quite well; their role in the nature, laboratory experiments and practical applications is explored in thoroughly. Detailed descriptions of these properties can be found in numerous textbooks and manuals on atomic physics edited in various countries of the World. However further advances in the scientific research is accompanied with progressive replenishment of the family of atomic physics objects. Many of those objects are well known to specialists, however the relevant information hardly can be found even in manuals and textbooks of recent time. We call these objects “exotic” ones, while many of them not only are described in detail in the modern scientific literature but also have found their technology applications. Aiming to overcome this contradiction there was edited a manual [1], where the information on the atomic physics objects not yet included into modern textbooks is brought together. The present article contains a survey of problems related to modern objects of atomic physics which attract the attention of researchers and high technology engineers. Physical properties, methods of production and exploration as well as approaches to the applied usage of new contemporary objects of the atomic physics have been reviewed shortly.

2. Negative ions

Electron affinity. Interaction of an electron with a neutral atom or molecule at distances exceeding a characteristic size of such a particle results in the attraction. This is caused by the formation of an induced electrical dipole moment of the atomic particle under the action of the electrical field of the electron. The interaction potential of electron and a neutral particle is described by the relation

\[ U(r) = -\frac{\alpha e^2}{2r^2}, \]

where \( \alpha \) – is the polarizability of the atomic particle, \( e \) is the electron charge and \( r \) is the distance between the electron and the atomic particle. At distances \( r \) comparable to the size of atomic particles the electron is experienced to a repulsion due to Coulomb interaction with bound electrons belonging to the atomic particle. Therefore the interaction of an electron with a neutral atomic particle is characterized by a potential well, which can contain one or several electron bound states. If one of these states is occupied by electron, the atomic particle is negative ion. The polarization attraction between an electron and an atomic particle is relatively low, so that the electron binding energy in negative ions, called as the electron affinity (EA) is notably lower than the typical electron binding energy in neutral atomic particles. Table 1 presents the values of EA for some atoms and simplest molecules. One should note that rare gas atoms and some molecules (e.g. N\(_2\)) do not form negative ions, since the potential well formed at the interaction of such particles with electron is too shallow.

Mechanisms of negative ions formation. The process of formation of a negative ion is called as the electron attachment. This process proceeds as a result of a collision between an electron and an atomic particle. For the
formation of a negative ion it is necessary to provide the removal of energy released at the electron attachment. One of the mechanisms of such a removal relates to the light quantum emission

\[ A + e \rightarrow A^- + h\nu. \]  

(2)

Such a process is called as the **photoattachment**. Particularly this process occurs in the solar atmosphere where the negative ion H⁻ is formed. The optical emission due to this process makes the main contribution into the spectrum of solar radiation. One should note that the cross section of the process (2) is rather low (~ 10⁻²² cm²) so that this process is usually not considerable in laboratory plasma conditions and manifests itself only in space systems such as the solar photosphere.

| Ion | H⁻ | He⁻ | Li⁻ | C⁻ | C⁺ | O⁻ | Na⁺ | K⁺ | Rb⁺ | F⁻ | Cl⁻ | Br⁻ | I⁻ |
|-----|----|-----|-----|----|----|----|-----|----|-----|----|-----|-----|----|
| EA, eV | 0.75 | 0.07 | 0.62 | 1.26 | 1.46 | 0.54 | 0.50 | 0.49 | 3.4 | 3.6 | 3.36 | 3.1 |

Another mechanism of the energy removal at the electron attachment relates to the dissociation of the molecular ion formed as a result of the interaction of an electron and a molecular ion formed

\[ AB + e \rightarrow A + B. \]  

(3)

Such a process is called as the **dissociative attachment** of an electron to a molecule. This process determines the electrical strength of the atmosphere. The electric breakdown of the atmosphere occurs if the rate constant of ionization of molecules comprising the atmosphere air exceed that for the dissociative attachment of electron to oxygen molecule. This condition is satisfied at electrical field \( E > 30 \text{ kV/cm} \).

Negative ions can be formed at not only pairwise but also at triple collisions so that the electron binding energy is removed by the third process participant which can be both neutral atomic particle (atom or molecule) and electron. This mechanism of ion formation prevails at relatively high gas pressure and low (or zero) electrical fields. Negative ions play very important role in the Earth atmosphere participating in processes of atmosphere electricity and making influence on formation of lightnings and thunderstorms. Since the lifetime of free electrons in the atmosphere is very short, the negatively charged particles are represented mainly by negative ions. Fig. 1 presents the kinetics of processes proceeding in B-layer of the Earth atmosphere with participation of negative ions.

**Fig. 1.** Illustration of the kinetics of processes proceeding in B-layer of the Earth atmosphere with participation of negative ions [2]

### 3. Excimer molecules

*Parameters of excimer molecules.* Rare gas atoms do not form molecules because their interaction with each another or with others atoms at the distances of the order of an atomic size has a repulsive character (see fig.2, line 1). However if one of the atoms is electronically excited, the formation of a bound molecular state is possible, so that the energy of this state exceeds that of the ground state (line 2). Such a molecule (quasi-molecule) exists only in an excited state and therefore is called as excimer molecule.
Fig. 2. Typical inter-nuclear distance dependences of the potential energy of a quasi-molecule consisted of rare gas atoms: 1) both atoms are in the ground state; 2) one of the atoms is excited.

The lifetime of excimer molecules is determined by the spontaneous radiation, the characteristic time of which accounts 1 – 10 ns. Excimer molecules contain a rare gas atom the excitation energy of which corresponds to a far UV spectral region, so that the radiation decay of excimer molecules is accompanied with emission of UV quanta. The light quanta emitted by excimer molecules escape freely from the system because there are not molecules able to absorb such quanta. The linewidth of the excimer molecule emission is many order of magnitude as large as the characteristic value inherent to atoms or molecules. This is caused by an arrangement of the potential terms shown on fig. 2. Table 2 presents parameters of some excimer molecules.

| Molecule | Ar₂ | Kr₂ | Xe₂ | ArF | KrCl | KrF | XeBr | XeCl | XeF |
|----------|-----|-----|-----|-----|------|-----|------|------|-----|
| Emission wavelength, nm | 126 | 146 | 172 | 193 | 222 | 248 | 282 | 308 | 352 |
| Emission linewidth, nm | 8   | 14  | 20  | 1.5 | 4    | 1   | 2.5  | 1.5  |     |

Excimer lasers. Since the lower state of the optical transition of an excimer molecule is never populated, the gas containing excimer molecules is always characterized by the inverse population on the relevant transition. Such a gas is a ready active media of the excimer laser. The distinctive peculiarity of such a laser relate to optical properties of excimer molecules. Firstly, excimer lasers are the sources of the coherent radiation in visible or UV spectral region. Secondly, due to relatively large linewidth of excimer molecules emission the wavelength of such lasers can be tuned within quite wide range (about 1% of the nominal value). Finally, due to effective mechanisms of excimer molecule formation such lasers possess relatively high efficiency.

Mechanisms of formation of excimer molecules. Dimer rare gas molecules (R₂ = Ar₂, Kr₂, Xe₂) are formed as a result of propagation of a high energy electron beam in a dense gas. Usually electron accelerator can be used for this aim while gas discharge is also utilized in some cases. At a propagation of fast electrons through a dense gas (pressure of several bars) practically all the energy is spent to the ionization of gas particles:

\[ R + e \rightarrow R^+ + 2e \]  

(4)

The atomic ions formed enter quickly into the conversion reaction

\[ R^+ + 2R \rightarrow R_2^+ + R \]  

(5)

At a gas pressure of several bars (N ~ 10²⁰ cm⁻³) the characteristic conversion time \( \tau_c \approx (kN^2)^{-1} \sim 10^{-10} - 10^{-9} \) s.

Then rare gas molecular ions enter into the dissociative recombination reaction

\[ R_2^+ + e \rightarrow R + R^* \]  

(6)

which results in formation of excited atoms R*, that recombine in triple collisions

\[ R^* + 2R \rightarrow R_2^+ + R \]  

(7)

with formation of dimer molecules \( R_2^+ \).

Excimer molecules consisted of a rare gas atom and halogen atom are form as a result of the harpoon reaction occurring in a mixture of haloid containing molecules (e.g. F₂, Cl₂, Br₂, SF₆ etc)

\[ R^* + X_2 \rightarrow RX^* + X \]  

(8)

In accordance to the harpooning mechanism, the weakly bound electron, like a harpoon, is captured to a state of the negative ion \( X_2^- \)

\[ R^* + X_2 \rightarrow R^+ + X_2^- \]  

(9)

and then the unlike ions attract with each other which results if formation of an excimer molecule RX*. Excited atoms R* necessary for performing the harpoon reaction (8) are formed in a dense gas either in result of the electron beam propagation or in result of pulsed discharge ignition.
4. Multi-charged ions.
Multi-charged ions form in result of detachment of several electrons from atom. The simplest case for analysis corresponds to the situation when only one electron is remained while the rest electrons are detached. In this case the ion is hydrogen-like and the energy spectrum of such an ion is expressed by the known Rydberg formula

\[ E_n = -\frac{Z^2n^2\hbar^2e^4}{2\pi^2\hbar^2m_e^2} \times \frac{2^2\text{Ryd}}{n^2}. \]  

(10)

Here \( Z \) is the charge of the nucleus, \( n \) — is the principal quantum number. Formula (10) has an approximate character if the multi-charged ion contains not one but several \( (n) \) electrons. In this case formula (10) should contain \( (Z-n) \) instead of \( Z \). On condition \( Z - n \gg 1 \) the interaction potential of the valent electron with the nucleus exceeds that for the electron-electron interaction, and an excite multi-charged ion is similar to a hydrogen-like one. As is seen, the electron state energies in hydrogen-like multi-charged ion differ from those in hydrogen atom by \( Z^2 \). Correspondingly the wavelengths of optical transitions in such an ion are by \( Z^2 \) shorter than those for transitions between the relevant excited state of hydrogen atom. Using the quantum mechanical approach it is easy to prove that the characteristic size of a multi-charged ion \( <r> \), determined as the average distance between the electron and nucleus, decreases with the rise of \( Z \)

\[ <r> = \frac{3}{Z} \]  

(11)

The dependence of the lifetime for radiation transitions depends on the charge \( Z \) as follows:

\[ \tau \sim Z^{-4}. \]  

(12)

The interest to production and investigation of multi-charged ions is stimulated by the development of microelectronics which requires for a constant miniaturization of size of elements incorporated into integral schemes. It can be reached particularly by the use of UV radiation sources wavelength of which should be decreased constantly. Thus the radiation with wavelength within the range of 10 — 20 nm can be obtained using hydrogen-like multi-charge ions with \( Z = 10 — 20 \). In this connection the problem of design of X-ray laser emitting in the wavelength range 10 — 20 nm arises. For operation of such a laser the generation condition should be met, in accordance with which the product of the amplification coefficient

\[ \cdot \frac{\lambda^2N_2}{\Delta \omega} \]  

(13)

by the length of the active media \( L \) exceeds the value of the order of unity. Here \( \lambda \sim Z^2 \) is the transition wavelength, \( \Delta \omega \sim <r>/\lambda \sim Z^2 \) is the Doppler line width of the transition, \( \tau \sim Z^{-4} \) is the radiation lifetime, \( N_2 \) is the population of the upper level of the laser transition. One can see that the generation condition for X-ray laser is about \( Z^2 \) times stronger than that for a laser on the basis of neutral atoms. For this reason not X-ray lasers but rather non-coherent sources of X-ray radiation are used as the main tool for treating nanoelements of electronics. To obtain a multi-charge ion an atom should get a large quantity of energy. Thus the minimum energy which is necessary for formation of the multi-charged ion with \( Z = 20 \) accounts as 2.5 keV, while for the ion with \( Z=30 \) this quantity is estimated as about 200 keV. Such a high-energy input can be reached either in conditions of a high temperature plasma formed at irradiation of a solid state target with high intense laser radiation or in result of propagation of an ion accelerated in a strong electrical field through special membranes where it loses sequentially its outer electrons.

5. Rydberg atoms
Parameters and properties of Rydberg atoms. Rydberg atom is a highly excited atom with the principal quantum number of the weekly bound electron \( n \gg 1 \). The weekly bound electron in a Rydberg atom is located quite far from the nucleus comparing to others electrons belonging to the atom. Its average distance from the nucleus exceeds by about \( n^2 \) times the characteristic radius of the electron orbit in a not excited atom. The behavior of such an electron is weekly sensitive to details of the structure of the atomic rest; therefore many properties of a Rydberg atom are similar to those of a highly excited hydrogen atom. In essence, the main parameter determining those properties is the principal quantum number of the weekly bound electron \( n \), while such properties of the atomic rest as the orbital moment and spin do not practically influence on the properties of the weekly bound electron. Specifically the binding energy of such an electron is expressed approximately through the Rydberg formula

\[ E_n \approx -\text{Ryd}/n^2. \]  

(14)

whence it follows that the distance between the neighboring levels is estimated as

\[ \Delta E_{n+1} \approx 2\text{Ryd}/n^3. \]  

(15)

This means that radiation transitions between neighboring states of a Rydberg atom correspond to not optical, as is in the case of ordinary excited atoms with \( n \sim 1 \) but rather to a far infrared or even microwave region of electromagnetic oscillations.
The dependence of parameters of a Rydberg atom on the principal quantum number can be estimated using the quantization rule, in accordance with which the momentum of an electron oscillating with the velocity $v$ over the orbit of radius $r$ can have only the value multiple of the Planck constant $\hbar$:

$$L_n = mv_nr_n = n\hbar.$$  \hfill (16)

On the other hand, the oscillating electron is experienced to a centrifugal acceleration $a = v^2/r_n^2$, the force of which $ma$ is balanced by the Coulomb interaction force $e^2/r_n^2$. This result in

$$v_n = \frac{e^2}{n\hbar} \frac{r_n}{me^2}.$$  \hfill (17)

Therefore the electron orbit radius in a Rydberg atom increases proportionally to $n^2$. It means that the density of a substance consisted from Rydberg atoms decreases proportionally to $n^{-6}$. For example, the density of a hypothetical material consisted of Rydberg atoms with $n \sim 100$ is as low as 12 orders of magnitude comparing to that of water.

The electron rotation period is estimated as the ratio of the orbit radius $r_n$ to the electron velocity $v_n$ which is proportional to $n^3$. Parameters of ordinary and Rydberg atoms are compared in Table 3.

| Principal quantum number | Binding energy, eV | Inter-layer distance, eV | Size, cm | Electron precession time, s | Lifetime, s |
|--------------------------|------------------|------------------------|---------|--------------------------|-------------|
| Ordinary atom            | $n=1$            | 5                      | 1       | $10^{-8}$                | $\sim10^{-16}$ | $\sim10^{-8}$ |
| Rydberg atom             | $n=1000$         | $\sim10^{-5}$          | $10^{-8}$| $10^{-3}$                | $\sim10^{-7}$ | $\sim1$ |

**Production of Rydberg atoms.** Rydberg atoms are produced in a laboratory as a result of sequential excitation of atoms by lasers of different wavelengths. The scheme of such an experiment is presented on Fig. 3. A beam of ground state atoms $A$ propagates from the atom beam source $S$ into a camera where it is irradiated by two lasers ($L_1$ and $L_2$) whose wavelength correspond to the transition into a Rydberg state of the atom. The Rydberg atoms are detected applying the electrical field which promotes the ionization of atoms. At a fixed value of the electrical field only atoms with the specific principal quantum number $n$ can be ionized for the time of flight through the region under the field.

Estimate the maximum quantum number $n$ reachable at utilization of the above-described method of Rydberg atom production. For this aim the inter-layer distance $\Delta E_{n,n-1} \approx 2\hbar r_n^3$ should be compared with the absorption linewidth that is determined by the Doppler broadening $\Delta \omega = 2\pi<\nu>\lambda$. Here $<\nu> \sim (T/M)^{1/2}$ is the average thermal velocity of atoms, $\lambda$ is the wavelength. The comparison results in

$$n_{\text{max}} \sim \frac{(\text{Ry} \lambda M^{1/2}/\hbar T^{1/2})^{1/3}}{}.$$  \hfill (18)

Substituting (in atomic units) the typical values $\lambda \sim 10^4$, $T = 10^{-3}$, $M = 10^4$, one obtains $n_{\text{max}} \sim 1000$. Rydberg atoms with such high values of the principal quantum number have been already observed recently.
stimulated emission of those atoms on the transition \( 63p_{3/2} \rightarrow 61d_{1/2} \) with the wavelength 13.95 nm. The maser effect occurrence is detected by the resonance decreasing of the ion current on the detector as a result of a fine tuning of the resonator for the transition frequency. The ionization of Rydberg atoms Rb \( 63p_{3/2} \) is performed by the stationary electrical field of 20 B/cm. Calculations performed indicate that at such a field strength the ionization rate for Rb\( 63p_{3/2} \) exceeds about 7 times that for \( 61d_{1/2} \).

A striking feature of the above-described experiment is that the maser effect occurs at very low beam intensity. The estimation shows that the average number of atoms located inside the resonator in each time moment does not exceed 0.06. Therefore only one Rydberg atom is sufficient for the maser operation. This conclusion is of a great importance for development of the quantum electrodynamics studying peculiarities of the interaction of radiation with substances.

![The schema of the detector of microwave radiation](image)

**Fig. 4.** The schema of the detector of microwave radiation

One more example of the effective usage of Rydberg atoms is a detector of microwave radiation. The operation schema of such a device is shown on fig. 4. Rydberg atoms Na\( (22D) \) are formed as a result of subsequent transitions Na \( 3S_{1/2} \rightarrow 3P_{1/2} \rightarrow 22D \) stimulated by frequency tunable lasers at wavelengths of 589 and 415 nm. Interaction of the Rydberg atoms with the thermal radiation under investigation results in transition to the neighboring state \( 23P \). Such transitions are detected due to the selective ionization of atoms Na\( (23P) \) in a stationary electrical field. Therefore the measurement of thermal radiation is possible due to high sensitivity of Rydberg atoms to the microwave radiation. Specifically, such a sensitivity has been used for registration of the relict radiation that contains an information on the Big Bang initiated the evolution of the Universe.

### 6. Clusters

![Mass spectra of clusters](image)

**Fig. 5.** Mass spectra of clusters: a)Clusters of rare gases formed at gas exhausting through a nozzle; b)mass-spectrum of clusters \( Mg_n \). The magic numbers of clusters are shown.

Clusters hold an intermediate position between the molecular and condensed state of the substance [4]. In distinction of a bulk condensed substance, the physical and chemical characteristics of a cluster depend on the number of particles or on its size in non-monotone manner. An example of such dependence is the energy accounted for one particle. The maximum stability of the cluster corresponds to the minimum value of the energy. Therefore the information on the cluster stability is contained in the mass-spectra of cluster beams. Non-monotone dependence of the energy accounted for one atom on the cluster size is reflected on the non-monotone character of the cluster mass-spectra. The peaks in mass-spectrum correspond to the maximum cluster stability. Some examples of such non-monotone mass-spectra are shown on Fig.5. The numbers of particles in clusters corresponding to maxima in the spectra are called “magic numbers”. The set of magic numbers characterizing clusters of some element determine the structure of cluster. Thus the set of the magic numbers \( n \) of clusters \( Mg_n \) shown on fig. 5b imply the icosahedral structure of clusters.
There exist two types of clusters: gaseous and solid state ones. The gaseous clusters are consisted of atoms or molecules of a substance that is in gaseous state at normal conditions. Such clusters form as a result of cooling. Usually it is performed by the expansion of the gas through a gas dynamic nozzle. The lower gas temperature and the higher gas pressure the more intensive the cluster formation proceeds and the bigger the cluster sizes. Depending on the parameters of the nozzle, one can obtain the clusters of practically any size. The “solid state” clusters are produced as a result of an action of an intense energy source onto a solid state surface. High power lasers or electron (ion) beams are usually used as an intense energy source. Heating the surface due to irradiation results in vaporization of the material. The material flow exhausting from the surface contains along single atoms also clusters of various size and some quantity of microscopic droplets.

- Many clusters possess fractal structure. The main feature of such structures is their self-similarity, i.e. invariability of the structure at enhancement of their size. Fractals have a fractional dimension that determines the interconnection between the size and the mass of the cluster. This interconnection can be expressed through the relation

\[ N = R^D, \]  

where \( N \) is the number of particles in a cluster, \( R \) is the radius of the cluster and \( D \) is its fractal dimension. One should not that for common bulk materials \( D = 3 \).

*Fig. 6* presents micro-images of 3D fractal clusters of Fe and Au, as well as the results of the measurements of the dependence of the mass of Au clusters vs. its size used for determination of the fractal dimension [5].

![Fig. 6. Micro-images of 3D fractal clusters of Fe (a) and Au (b) as well as the measured dependence of the cluster mass on its size (semi-logarithm scale) used for determination of the fractal dimension of the clusters (c). [5]](image_url)

Basic research in the field of production of clusters and investigation of their physical and chemical characteristics is stimulated by applications of clusters in micro- and nanoelectronics. Thus deposition of clusters of several nanometers in size onto a substrate results in formation of quantum dots electronic characteristics of which (carriers concentration, forbidden gap width etc) differ considerably from those for the substrate. Therewith the \( p-n \) - junction of recordable small size can be obtained which offers a possibility for further miniaturization of electronic devices.

7. Carbon nanostructures

In last decades we have become witnesses of the appearance and development of new branches of research in the field of the structures of substances. These branches can be pooled under the common term “nanotechnologies. The distinctive feature of subjects of nanotechnologies is the dimension effect. This effect manifests itself in a dependence of properties of the subject on its size. As it was noted above (pt. 6) the dimension effect is inherent to clusters, the stability of which depends on the number of atoms or molecules comprising the cluster. Carbon nanostructures present the most deeply studied set of subjects of the nanoworld. Their discovery and investigation makes a stimulating influence onto the progress in the field of nanotechnologies.

The structures of the main carbon modifications are shown on *Fig. 7*. At the end of XX and at the beginning of XXI century the class of known carbon structures such as graphite and diamond was replenished by new ones such as fullerenes, carbon nanotubes and graphene as well as their derivatives. The studies performed indicate a diversity of physical and chemical characteristics inherent to those structures. Intense efforts addressed to production, exploration and applied usage of carbon nanostructures are undertaken in many laboratories of the world.
Fig. 7. The structure of the main carbon modifications

Fullerenes. Fullerenes were discovered occasionally. The authors of this discovery tried to reproduce carbon clusters responsible for the absorption of the optical radiation by inter-star nebulae. They irradiated crystalline graphite by intense laser in He atmosphere and measured the mass-spectrum of carbon clusters exhausted. This mass-spectrum contained peaks $C_n$ with $n = 60$ and $n = 70$ which indicated the enhanced stability of clusters of the relevant size. Such an observation was explained supposing the extraordinary structure of such clusters in accordance with which carbon atoms are placed in a symmetric manner on a closed surface having a spheroid or spheroidal structure. The surface is consisted of regular hexagons and pentagons with carbon atoms in their vertices. The structure of the most spread clusters $C_{60}$ and $C_{70}$ is shown on Fig. 8a, b. The image of the molecule $C_{60}$ obtained by means of the field ion microscope [6] is shown on fig. 8c. Such a structure contains 12 pentagons and a number of hexagons, depending on the cluster size. The structures of such a type were called as fullerenes, by the name of the famous American architect Buckminster Fuller who firstly used the similar structures for building cupola. While fullerenes were discovered as clusters the further studies resulted in the conclusion that such structures possess the properties inherent to molecules. The discovery of fullerenes was noted by the Nobel Prize in chemistry in 1996.

The most symmetric and the most stable fullerene molecule consisted of 60 carbon atoms ($C_{60}$). In such a molecule each pentagon borders to 5 hexagons while each hexagon borders alternately with three hexagons and three pentagons. All the carbon atoms belonging to such a molecule are found in the vertices of two hexagons and one pentagon is $C_{60}$ therefore all the atoms are characterized by the unique chemical state. One more confirmation of the unique structure of fullerene molecules is the result of measurement of the nuclear magnetic resonance of molecules $C_{60}$, $C_{70}$ and the mixture $C_{60} + C_{70}$ presented on Fig. 9. Existence of the only one line in the NMR spectrum of $C_{60}$ molecule indicates that all the carbon atoms in this molecule are found in the same chemical state. The NMR spectrum of $C_{70}$ contains four lines so that this molecule contains four types of carbon atoms found in different chemical states. The NMR spectrum of the mixture $C_{60} + C_{70}$ contains five lines.

While the fullerenes were firstly synthesized in experiments on laser sputtering of a crystalline graphite in He atmosphere, the most effective method of their production in macroscopic quantities is based on the usage of the electric arc with graphite electrodes in He atmosphere. The fullerene production procedure involves several stages. On the first stage a fullerene containing soot is produced in an arc discharge with graphite electrodes in He atmosphere. On the second stage fullerenes are extracted from the soot by means of a solvent for which such solvents as benzene, toluene etc are usually used. Fullerenes is the only soluble carbon modification, that is why they are dissolved in the solvent while the other components of the soot are not dissolved. For the separation of fullerenes the solvent is evaporated which results in formation of tiny fullerene crystals. These crystals contained a mixture of fullerenes of various sorts ($C_{60}$, $C_{70}$ and some small admixture of higher fullerenes such as $C_{76}$, $C_{84}$ etc). On the third stage of the fullerene production procedure the separation of fullerene molecules of different sorts is performed. This procedure is based on liquid chromatography. Such an approach uses a difference in the sorption ability of fullerene molecules of different sorts in relation to the some sorbent. A fullerene mixture solution is passed through a solvent, and fullerene molecules are adsorbed by sorbent pores. If a pure solvent is passed through the sorbent filled with fullerene molecules then fullerene molecules of different sorts are extracted from the sorbent with different rate. The lighter fullerene molecule the sooner it is extracted from the sorbent. Therefore the solvent containing fullerene molecules of various sorts is enriched in relation to lighter fullerene molecules comparing to
the initial solution content. Repeating the procedures of sorption and desorption one can obtain high purity fullerenes of any sort.

Fig. 8. The structure of the most spread fullerene molecules: a) C\textsubscript{60}; b) C\textsubscript{70}; c) the image of the molecule C\textsubscript{60} obtained by means of the field ion microscope [6]

Fig. 9. NMR spectra of C\textsubscript{60}(a), C\textsubscript{70}(b) Рис. 27. Спектры ЯМР молекул фуллеренов и смеси C\textsubscript{60} + C\textsubscript{70}(c)

**Fullerenes in Solutions.** Since fullerenes are the only soluble carbon modification, peculiarities of their behavior in solutions are of a great scientific and practical interest [7]. One of such peculiarities relates to the cluster origin of fullerene solubility. Results of investigations imply that fullerenes in solutions form clusters consisted of a number of fullerene molecules. As the temperature increases the clusters tend to destroy. Such a behavior results in a non-monotone temperature dependence of the solubility of fullerenes. An example of such dependence is presented on **fig. 10** where the experimentally observed dependence is compared with results of calculations performed within the frame of the droplet model of clusters. The analysis of non-monotone character of the temperature dependence of the fullerene solubility permits one to evaluate the fullerene cluster size distribution function in solutions.

Fig. 10. Temperature dependence of the solubility of fullerene C\textsubscript{60} + in hexane (times 55); □ - in toluene (times 1.4); ◼ - in C\textsubscript{2}H\textsubscript{4}; • - in xylene. The solid line shows the results of calculations assuming the cluster origin of solubility using the droplet model of clusters [7].

Along with relatively small clusters it is possible the formation of large size fullerene clusters in solution. Such clusters contain hundreds thousands of fullerene molecules. These clusters are rather unstable and destroy at a light shaking the solution. Growth of such clusters lasts for several dozen days months which results in clusters of about 200 nm in size and 2\times10\textsuperscript{5} in the number of fullerene molecules. Large clusters have a fractal structure with the fractal dimension D \approx 2.

**Endohedral fullerenes.** The inner size of a fullerene cage (about 0.7 nm) considerably exceeds the characteristic diameter of atoms and simple molecules (0.1 ±0.4 nm) therefore it is possible to insert one or several atomic particles inside the fullerene molecules. Fullerenes molecules encapsulating one or several atomic particles (atoms or molecules) have been called endohedral compounds (or endohedrals). These compounds are symbolized by the formula Mn@C\textsubscript{n}, where M is the encapsulated atom or molecule and the subscripts m and n show the number of such atoms and carbon atoms in the fullerene molecule, respectively. This notation permits us to distinguish...
between an endohedral molecule and conventional (exohedral) chemical compounds which (in the case of fullerenes) are designated by the standard symbol M\textsubscript{m}C\textsubscript{n}. The interest to endohedral fullerenes is caused by their unique physical and chemical properties and some perspective applications [8].

Fig. 1 presents the structure of some endohedral fullerenes. Investigations indicate that a metal atom incorporated into a fullerene cage tends to attract to the inner surface of the cavity. Therewith the main distinctive peculiarities in optical spectra of the endohedral molecules are determined by the valence of encapsulated atoms rather than by the structure of the fullerene shell. The above-formulated conclusion has a common significance. This relates to the behavior of valence electrons belonging to metal atoms encapsulated inside the fullerene cage, which are not localized on the atom orbits, but arranged outside the fullerene surface. The distinction between the optical absorption spectra of endohedral molecules La@C\textsubscript{82} and Y@C\textsubscript{82} and those of similar compounds with encapsulated metal atoms of Group II can be explained in the same manner. It is caused by the difference in the valence of metal atoms and respectively in the number of electrons transferred from an atom to a cage. The structure of an endohedral metal fullerene can be expressed in the generalized form as $M_{k}^{m}C_{n}^{m-k}$ where $k$ is the number of encapsulated metal atoms, $m = kv$, and $v$ is the valence of the metal atom. It should be kept in mind that the fullerene shell has seemingly no more than six electron vacancies, which limits the total number of transferred electrons $m$. However, there is experimental evidence of the existence of such charge transfer complexes as $(La^{3+})@C_{80}^{6-}$, $(La^{3+})@C_{72}^{6-}$ and $(Sc^{2+})@C_{84}^{4-}$ [9, 10].

![Fig. 11 The structure of some endohedral fullerene molecules: a)Ca@C\textsubscript{82}; b)Sc\textsubscript{2}@C\textsubscript{82}; c)N@C\textsubscript{60}](image)

Endohedral fullerene molecules are produced either during the fullerene synthesis process or through filling the ready fullerene molecules with atoms (ions). Thus endohedral fullerene molecules containing La atoms were produced in an arc discharge with graphite electrodes. A hole of 270 mm in length and 10 mm in diameter was drilled out in a cylindrical graphene rod of 15 mm in diameter. This hole was filled with La\textsubscript{2}O\textsubscript{3} powder. The molar fraction of La in the anode material accounted 1.6 %. The arc discharge was burned in He atmosphere at a pressure of 180 – 220 Tor, current of 95 – 115 A and a pressure of 20 – 25 V.

![Fig. 12. The schema of the setup for production of endohedral fullerene molecule N@C\textsubscript{60} through the simultaneous deposition of C\textsubscript{60} onto a substrate and irradiation of the substrate with nitrogen ions. 1 - nitrogen ion source; 2 - electrostatic lens; 3 - substrate for fullerene deposition; 4 - device for controlling the coating thickness; 5 - fullerene beam source; 6 - vacuum camera; 7 - water cooling](image)

Another approach to production of endohedral fullerene molecules is based on principles of ion implantation. This approach is illustrated on fig. 12. Fullerene molecules are experienced to the irradiation by the ion beam of the relevant element to be intercalated. Some ions penetrate inside the fullerene molecule cages which results in formation of the endohedral structure. This approach is characterized by a rather low yield ($\sim 10^{4}$) therefor a pure material can be obtained after the
recurring action of the chromatography procedure.

**Carbon nanotubes.** Carbon nanotubes (CNTs) are elongated cylindrical structures of between one and several nm in diameter and up to several μm in length consisted of one or several hexagonal graphite layers rolled into a tube. Usually a nanotube is terminated with a hemispherical tip that can be considered as a half of a fullerene molecule. However, in distinction of fullerenes which present a molecular carbon modification, CNTs combine the properties of both molecular object and a condensed phase, therefore they can be considered as an intermediate state of the substance. Such a peculiarity attracts a growing interest from researchers whose activity is addressed to the study of basic properties of such exotic objects in various situations [11].

![Fig. 13. The structure of CNTs of various chirality: A – zigzag, B – armchair and C – a nanotube with an arbitrary chirality.](image)

**The structure of nanotubes. Chirality.** A nanotube can be obtained as a result of rolling of the a hexagonal surface at different angles. The orientation angle determines the chirality of a nanotube. The chirality is one of the main characteristics of a nanotube because it determines its electronic properties. The chirality is denoted by the chirality indices \((m, n)\), which determine the diameter of a nanotube \(D\):

\[
D = \sqrt{m^2 + n^2 + mn} \sqrt{3d_0} / \pi.
\]

Here \(d_0 = 0.142 \text{ nm}\) is the distance between the neighboring layers in graphite. The chirality indices denote the coordinates of the point on the hexagonal plane which coincides with the origin at rolling the surface into a cylinder. The chirality indices can be expressed also through the orientation angle \(\alpha\) of the hexagonal plane relative to the nanotube’s axis:

\[
sin \alpha = \frac{3m}{2\sqrt{(n^2 + m^2 + mn)}}.
\]

Depending on the chirality, three types of nanotubes are distinguished: A – zigzag, B – armchair and C – a nanotube with an arbitrary chirality. **Fig. 13** presents the nanotubes of various chirality.

A typical diameter of single-walled nanotubes accounts 1 – 2 nm while their length can reach a millimeter size. **Fig. 14** presents the images of single walled CNTs of different chirality obtained by means of a scanning tunneling microscope. These images are compared with those obtained by computer simulations.

![Fig. 14. The images of single walled CNTs obtained through STM observations (a) and computer simulations performed for nanotubes with the chirality indices (13, -1) and (15,3) (b).](image)

Singe-walled CNTs are usually bound into bundles contained up to several tens of nanotubes. The stability of the bundles is provided due to the van der Waals attraction so that the distance between the neighboring nanotubes in a bundle is close to 0.34 nm. Carbon nanotube can consist of several walls so that the inter-wall distance accounts also 0.34 nm. CNT can form branched structures which suggests a possibility of formation of CNT-based electrical...
circuits. Such circuits can be fabricated through the electron-beam welding. An example of such an approach is given on Fig. 15 where the formation of an X-like junction of two CNTs by electron-beam welding is shown. A point of crossing two nanotubes is experienced to the electron beam action of a proper intensity which results in the formation of a stable junction between two nanotubes.

**Peapods.** The diameter of a single-walled CNT exceeds usually 1 nm. Therefore a nanotube can be filled with fullerene molecules [8]. Such an endohedral structure is named as peapod. Fig 16 presents microimages of some endohedral peapods obtained by means of a transmission electron microscope.

A miniature size of CNTs makes their registration and characterization to be very hard problem. An effective tool for the solution of this problem is Raman spectroscopy permitting one both to register the existence of CNTs on the basis of their Raman spectra and to state their diameter distribution. As any quantum object a nanotube is experienced to lattice vibrations which characteristics frequencies are determined by its structure. Specifically the nanotube/s diameter changes periodically and such a vibration mode is called as the radial breathing mode. The frequency of such a vibration is inversely proportional to the nanotube’s diameter which permits one to determine the diameter distribution of single walled nanotubes on the basis of the Raman spectrum. Such an approach is illustrated on Fig. 17, presenting the Raman spectrum of single-walled CNTs produced in an electrical arc with graphite electrodes with the use of Ni-Cr alloy as the catalyst.

Carbon nanotubes are produced either as a result of graphite sputtering in an arc discharge with graphite electrodes or at a thermal decomposition of carbon containing gases in the presence of catalysts. Nanoparticles of transition metals (Fe, Ni, Co) and some other metals are used as catalysts. The latter approach is called as chemical vapor deposition or CVD. In accordance to this approach, illustrated on Fig. 19, carbon containing gas is passed through a furnace where is paced a substrate with catalyst particles on its surface. As a result of decomposition of molecules on catalyst particles at enhanced temperatures (1000 – 1300 K) carbon atoms are generated which results in formation of nanotubes that grow out of the catalyst particles. Usually the diameter of nanotubes is about 1.5 – 2 times lower than the size of particles. If the catalyst particles are placed in a regular manner over the substrate surface catalyst the vertically aligned nanotubes form a forest-like massive.

Carbon nanotubes are distinguished by extraordinary physical and chemical properties. The main peculiarity of such objects as nanotubes relates to the existence of quantum dimension effects. These effects manifest themselves

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**Fig. 16.** Microimages of endohedral peapods obtained by means of a transmission electron microscope: a)Gd@C₈₂; b)Ca@C₈₂.

**Fig. 17.** The Raman spectrum of CNTs and the diameter distribution: a) total Raman spectrum measured by means of a laser with $\lambda = 514.5$ nm: I – radial breathing modes; II tangential modes; b) a magnified part of the spectrum related to the radial breathing modes. The relevant values of nanotube’s diameter are shown at peaks.

**Fig. 18.** Illustration of the CVD method of CNT production.
in dependence of physical and chemical characteristics of CNTs on their size. For example both the thermal and electric conductance of CNT does not depend on its length. This can be seen from Fig. 19 presenting the dependences of the thermal ($G_{th}$) and electric $G_{e}$ conductance on the CNT’s length. Independence of these parameters on the nanotube’s length means that both the thermal and electric conductivity defined through the relations

$$\lambda = \kappa S/l; \quad \sigma = G S/l$$ (22)

do depend on the nanotube’s size. As is known, macroscopic objects do not possess such dependence. Here $S$ is the cross section area of a nanotube, $l$ is its length.

**Fig. 19.** Dependences of the thermal conductance (1) and electric conductance (2) on the nanotube’s length [12].

The above-described peculiarities in dependences of the thermal and electric conductance on the nanotube’s length can be considered as a manifestation of the dimension effect inherent to nanotubes and other nano-objects. In the case of defectless nanotubes both the electron and heat transport has a quantum, ballistic character. The ballistic electric conductance is expressed by a relation

$$G_e = \frac{4e^2}{\hbar} = \frac{1}{6.45} \text{k}\Omega,$$ (23)

which corresponds to the ballistic resistance

$$R_e = 6.45 \text{k}\Omega.$$

The ballistic transport of the charge and heat occurs for rather short nanotubes the length of which is shorter than the characteristic mean free path for electrons (in the case of electric conduction) or phonon (in the case of heat conduction). Otherwise the electric (thermal) conductance decreases with the nanotube’s length as is the case for macroscopic objects.

**Electronic properties of CNTs** are determined by their geometry parameters (diameter and chirality). Thus single walled nanotubes possessing the armchair structure (Fig. 14b) demonstrate the metallic conduction. Usually the number of such CNTs accounts about one third of all the nanotubes synthesized. The nanotubes with arbitrary chirality indices are semiconductors for which the forbidden gap width is determined by both the diameter and the chirality indices. **Fig. 20** presents the dependences of the forbidden gap width on the nanotube’s radius calculated and measured for nanotubes of different chirality.

**Fig. 20.** Dependences of the forbidden gap width on the nanotube’s radius calculated (a) and measured (b) for nanotubes of different chirality.

Existence of defects in the nanotube structure changes its electron characteristics. The most spread type of structural defect is the Stone-Wells defect (pentagon-heptagon) incorporated into the hexagonal CNT structure (**Fig. 21**). Such a defect separates the regions of the nanotube possessing different chirality and therefore with different forbidden gap width. For this reason defect CNTs can be considered as natural heterostructures that can be used as elements of nanoelectronic circuits.

**Fig. 21.** Stone-Wells defect (pentagon-heptagon) incorporated into the regular hexagonal CNT structure and separating the regions of the nanotube possessing different chirality.
Carbon nanotubes possess unique **mechanical characteristics** [13]. Similar to macroscopic objects, CNTs are experienced to deformation under the action of mechanical loading. Fig. 22 presents some types of such deformations. The main parameter characterizing elastic properties of CNTs is the Young modulus defined as

\[ Y = \frac{\sigma}{\varepsilon} = \frac{F}{2\pi h \varepsilon}. \]  

(24)

Here \( \sigma \) is the specific loading, \( \varepsilon \) is the relative tension, \( F \) is the longitudinal force, \( h \) is the wall thickness. The inter-relation (24) between the loading and tension is one of the formulations of the **Hook Low**.

**Figure 22.** The main types of nanotube’s deformations [13]: (a) axial strain; (b) axial compression (diameter buckling); (c) symmetrical bending; (d) radial compression; (e) elastic deviation, and (f) Euler deformation (shell buckling).

The measurements performed imply extraordinary high strength characteristics of CNTs. The measured value of the Young modulus of CNTs reaches TPa level which exceeds the standard value for the most strong metal filaments by tens times. Such a high strength of CNTs is caused by a defectless structure of those. While the strength of macroscopic filaments is determined by the existence of defects, the defect content in nanotube can be negligible so that the strength of such a material is determined by the chemical bond energy of of the relevant carbon atoms.

Recordable strength characteristics of CNTs allow the fabrication of strong threads and textiles. Threads from nanotubes are produced with the use of standard approaches utilized in the textile industry. Such a technology is illustrated on **figure 23** presenting the microimages of CNT threads obtained as a result of spinning the yarn.

**Figure 23.** The yarn and threads spinned from CNTs. Top: a rope of 20 \( \mu \)m in diameter spinned of four threads; center: SEM image of spinning the thread from a multi-walled CNT array; bottom: the yarn of complex spinning.

Carbon nanotubes possess unique passing capacity. The passing capacity of CNTs for water \( Q \) is three orders of magnitude higher than that determined by the Poiseulle formula valid for macroscopic membranes

\[ Q = \frac{\pi R^4 \Delta p \varepsilon}{8 \mu L}. \]  

(25)

Here \( R \) is the channel radius, \( L \) is its length, \( \Delta p \) is the pressure drop. Such a high passing capacity of CNTs is caused by a smooth structure of their surface due to which the tangential velocity of water near the surface is not zero, which is not the case for macroscopic membranes having rough walls.

**Composite materials.** Unique electric and mechanical characteristics of CNTs offer a possibility for modification of polymer materials through inserting some quantity of CNTs into a polymer matrix. This imparts enhanced mechanical properties to the material and permits the production of polymer composites for a wide field of applications. Table 4 compares mechanical characteristics of some materials with the relevant data for polyethylene-based composite doped with 30% CNTs. As is seen due to high strength of CNTs inserting this material into polyethylene results in production of a composite with mechanical characteristics exceeding conventionally used materials.

| Material                  | CNTs(30%)/Polyethylene | High pressure polyethylene | Carbon fibers | Steel | Kevlar |
|---------------------------|------------------------|-----------------------------|---------------|-------|--------|
| Young modulus, GPa        | 162                    | 2.4                         | 181           | 200   | 90     |
| Breaking strength, GPa    | 6.6                    | 0.21                        | 1.5           | 0.62  | 3.6    |

**Table 4.** Comparison of mechanical characteristics of CNT-doped polyethylene with those for others materials.
Composite materials doped with a small quantity of conducting nanoparticles can conduct the electric current by the percolation mechanism, in accordance with which conducting paths form at reaching some critical concentration of the particles [14]. Calculations performed imply that the threshold value of the concentration of conducting particles \( \Phi_0 \) is inversely proportional to the aspect ratio of those particles (ratio of the length \( L \) to the diameter \( d \)) \( \Phi_0 \sim d/L \). Therefore the carbon nanotubes for which the aspect ratio reaches \( 10^3 - 10^4 \), for transformation of a polymer into a conductor even small quantity of CNTs (or the level of 0.01 – 0.1%) is sufficient. The dependence of the percolation conductivity on the filler content is given as follows

\[
\sigma = \sigma_0 (\Phi/\Phi_0)^t,
\]

where \( t \approx 2 \) – is the power index. In accordance with this dependence, a small excess of the additive content over the threshold the conductivity of the material increases by 10 – 12 orders of magnitude so that the initially isolating material becomes a conductor.

Emission properties of CNTs. Due to extraordinary high aspect ratio and good conduction carbon nanotube are effective source of the electron field emission [15, 16]. A potential barrier appears at applying an electrical potential onto a grounded conductor that can be overcome through quantum electron tunneling. This results in initiation of the electron field emission. The dependence of the emission current \( I \) on the electrical field in a vicinity of the conductor surface \( E \) is expressed through the Fowler-Nordheim equation

\[
j = C_1 \frac{E^2}{\phi} \exp \left( -\frac{C_2 \phi}{E} \right). 
\]

Here \( \phi \) is the electron work function, \( C_1 \) and \( C_2 \) are the coefficients depending on the geometry of the conductor. Figure 24 shows the typical current-voltage characteristics of CNT-based electron field emitter represented as the dependence \( \ln(V/V^3) \) vs \( 1/V \) (V is the applied voltage). The rectilinear shape of these dependences confirms valuability of the Fowler-Nordheim relation (27) within the range of 12 orders of magnitude for the emission current.

**Figure 24.** Typical current-voltage characteristics of the CNT-based electron field emitter of 1.1 μm in length and 8 nm in diameter. Triangles: CNTs before cleaning; rhombs: CNTs after cleaning.

The main distinctive feature of the electron field emission from CNTs relates to a high aspect ratio of those. Analysis imply that an elongated conductive object oriented along the direction of the electric field enhances the electrical field strength in a vicinity of its tip be a factor of the order of the aspect ratio of this object. Due to this property the carbon nanotubes for which the magnitude of the aspect ratio reaches about \( 10^3 – 10^4 \) are unique sources of the electron field emission. While for a notable emission from a conventional conductor the voltage of the order of several kV is necessary, for emission from CNTs several hundred volts is sufficient.

**Graphene.** Graphene is a 2D structure consisted of carbon atoms (figure 7) [17, 18]. In such a structure carbon atoms are placed into vertices of regular hexagons constituting hexagonal plane. The hexagon side in of 0.14 nm in length. Many properties of graphene are determined by the structure of its boundary. Some types of such a boundary are shown on figure 25. The structure of the graphene boundary is characterized by the chirality defined above. Transport characteristics of graphene are determined by structural defects some of which are presented on figure 26.

**Figure 25.** Illustration of the types of chirality of a graphene sheet boundary.

**Figure 26.** Structural defects in a graphene sheet: (a) fragment of a graphene sheet with an attached H radical(a); Stone-Walls defect (b), and vacancy defect (c).
According to the Landau-Peierls theorem, a regular flat 2D infinite structure cannot exist because the total energy of transversal vibrations goes to infinite. At first glance the fact of existence of graphene rules out this theorem, however this theorem remains to be true if take into account firstly a finite size of real graphene samples, and secondly deviation of the graphene structure from the flat one. This deviation has been observed in experiments with the usage of a scanning electron microscope the results of which are shown on figure 27. The measurements indicate Согласно измерениям, свободно подвешенный лист графена имеет волнистую поверхность с длиной волны около 1 мкм.

**Figure 27.** (a, b) The results of studying the structures of two graphene sheets suspended over a trench in an Si/SiO\textsubscript{2} substrate [23]. The boundary of the trench is marked by the brace on the left. Top: a topography image of graphene; bottom: dependence of the sheet height on the longitudinal coordinate restored on the basis of AFM measurements.

Along with graphene possessing 2D structure carbon atoms are able to form 1D chains. Such chains can be obtained from graphene as a result of action of a moderate intense electron beam. Sometimes such an action results in a chain connecting two fragments of the graphene sheet. This chain is rather unstable, it migrates along the sheet boundary and can destroy easily. **Figure 28** presents the results of numerical simulation of 1D carbon chain [20].

**Figure 28.** The structure of an 1D carbon chain determined by computer simulation [20]. The inter-atom distances are given in Å.

**Synthesis of graphene. Micromechanical exfoliation of graphite.** The first approach to the synthesis of graphite has been undertaken by the British researchers of Russian origin A. Geim and K. Novoselov [21]. Graphene samples were first separated through the micro-mechanical cleavage of graphite. In doing so, graphene sheets are separated from crystalline graphite either by rubbing small graphite crystals against each other or by means of an adhesive tape whose further dissolution in acid leads to separation of individual graphene sheets. Measurements have shown that this approach allows separation of single-layer graphene sheets about 10 mm in width and roughly 100 mm in length having an ordered structure. The above-described approach is characterized by a rather low productivity, however it results in the samples of the most perfect quality with minimum defect content.

**Synthesis of graphene by the chemical vapor deposition (CVD).** The CVD method is based on an ability of gaseous hydrocarbons to decompose on a surface of some metals with subsequent self-organization of carbon atoms into either nanotubes or graphene, depending on conditions. The usage of CVD procedure permits the production of macroscopic size graphene samples [22]. Usage of the CVD procedure permits the production of macroscopic size graphene samples.

**Figure 29.** Schematic of the roll-based production of graphene films grown on a copper foil [22].

The production of graphene sheets of recordable diagonal size (about 75 cm) described in [22] is illustrated on **Figure 29.** A copper foil is wound onto a quartz tube of 19 cm in diameter which is inserted inside a furnace of 20 cm in diameter. A mixture CH\textsubscript{4} + H\textsubscript{2} is pumped through the tube that is kept at a temperature of about 800 – 1000 °C. Decomposition of methane on the cupper surface results in dissolution of carbon atoms in cupper. Subsequent
slow cooling of the foil causes precipitation of copper atoms onto the foil surface and the formation of a graphene sheet. This sheet is transferred onto a PET (polyethylene-terephthalate) polymer film by means of flexible rollers at a temperature of 120 °C. Such flexible transparent conducting graphene sheets can be used as a basis for touch-screen monitors in notebooks and smartphones.

**Graphite oxidation (Hummers method).** One of the most effective approaches to the separation of graphite layers is based on the usage of chemical oxidizers. According to this approach, graphite layers are separated from each other in a liquid phase under the action of strong oxidizers such as oxygen and halogen molecules. The oxidation of graphite inner layers is accompanied with an enhancement of the inter-layer distance and corresponding decrease of the interaction energy between the layers. This facilitates the liquid phase separation of graphene layers which permits the synthesis graphene samples of about several μm in size. The graphite oxidation is performed with the use of the Hummers method which is known more than 60 years. Finely dispersed graphite is placed into an anhydrous mixture of concentrated sulfur acid, sodium nitrate and potassium permanganate. The oxidation of graphite is accompanied with the expansion of graphite and exfoliation which is facilitated due to a negative charge of some graphite oxide fragments. Subsequent treatment of the suspension through the ultrasonication and centrifugation results in removal of non-exfoliated graphite particles and other particles. Graphene oxide flakes are reduced either by chemical reaction (e.g. by hydrazine) or by thermal processing. The graphene samples produced through the above described methods are characterized by the existence of a large number of defects related to both functional groups CO-, O- etc and by occurrence of vacancies.

**Heat conduction of graphene.** Graphene possesses recordable high heat conduction coefficient. The thermal transport in graphene is due to the phonon propagation High thermal conduction of graphene is caused by the perfectness of its crystal structure which in its turn relates to a miniature size of graphene samples. The enhancement of graphene size is accompanied with an increase of the quantity of defects which present the scattering centers for phonons inhibiting their propagation. Miniature graphene sizes make the evaluation of thermal conduction of this object extraordinary complicated. One of the elegant approaches to this problem is illustrated on Figure 30. According to this approach, the local heating of a graphene sheet is performed by means of the Ar+ with λ = 0.48 μm, focused into a spot of about 1 μm in diameter. The temperature is determined on the basis of processing the Raman spectra of graphene which obey to a known temperature dependence.

![Figure 30. Schematic of the experimental setup for measuring the thermal conductivity of graphene](image)

![Figure 31. Comparison of the measured temperature dependence of the thermal conductivity of a graphene sheet lying on an Si/SiO2 substrate with the relevant data for pyrolytic graphite (PG) and with calculated results for suspended graphene (thick solid line) and graphene lying on a substrate (thin solid, dashed, and dashed-dotted lines). The calculations were performed using various model approximations.](image)
Figure 31 presents the results of measurements of the temperature dependence of the thermal conduction coefficient for graphene samples lying on SiO$_2$ substrate in comparison with the relevant data for pyrolytic graphite (PG), and model calculations for suspended graphene and graphene lying on the substrate. The calculations were performed under various model assumptions. A decrease of the thermal conduction with the temperature is caused by an enhancement of the number of phonons and related phonon-phonon scattering as well as with the enhancement of the cross section of phonon-phonon scattering with the rise of the temperature. If the graphene sample does not possess structural defects, the thermal conduction coefficient increases with the rise of the graphene sample size. This is caused by an enhancement of the number of phonon modes transporting the heat from the more hot region to another one. Conversely, increase in the defect content results in a decrease in the thermal conduction coefficient. This can be seen from Figure 32 presenting the dependences of the thermal conduction coefficient on the content of defects of various types.

![Figure 32](image)

**Figure 32.** The thermal conductivity of a defective graphene sheet $L = 1 \, \mu m$ in length as a function of the concentration on vacancies (a), and OH groups (b) calculated by the use of various approaches [18]

**Electrical field enhancement by a graphene sheet.** Graphene as a conductive object is able to enhance the electrical field. The maximum enhancement occurs in a vicinity of the border of the graphene sheet. This property makes the basis for operation of graphene-based electron field emitters. A model configuration of such an emitter is shown on Figure 33 [23]. Figure 34 present the results of calculation of the dependence of the electrical field amplification factor on the coordinate along the graphene sheet.

![Figure 33](image)

**Figure 33.** Model configuration of the graphene-based electron field emitter, where $D$ is the width, $h$ is the height, $a = 0.34 \, nm$ is the thickness.

![Figure 34](image)

**Figure 34.** (Color online) Dependence of the electric field amplification factor, $\beta$, upon the position along the edge of a graphene layer, $X$, calculated for samples of various heights.

Nonhomogeneous distribution of the electrical field amplification factor along the edge of the graphene sheet determines the shape of the current-voltage characteristic of the graphene-based electron field emitter. Figure 35 presents the results of calculation of this characteristic. The bend on this characteristic is caused by a sharply nonhomogeneous character of the dependence of the electrical field amplification factor on the coordinate along the edge of the graphene sheet (figure 34). At a relatively low electrical field the narrow edge regions having high amplification factor contribute mainly to the emission current. As the electrical field increases the contribution of the central region of the emitter enhances. This region has a lower amplification factor, however the emission area is higher for that. Figure 36 presents the dependences of the relative contribution of the two region of the graphene sheet into the total emission current. A bend of the current-voltage characteristic of the graphene-based electron field emitter obtained by numerical calculations and shown on figure 34 has been observed experimentally under the conditions close to those used in the above-presented calculations. The comparison of the model calculation results with the measured current-voltage characteristic (Figure 37) indicates the important role of edge effects determining the operation of the graphene-based electron field emitter.
Figure 35. Current-voltage characteristics of graphene-based emitters calculated (Fowler–Nordheim coordinates) for (a) samples 100 nm in width and with various heights and (b) samples 5 lm in height and with various widths (b). The inter-electrode gap is 0.1 mm.

Figure 36. Relative contribution of the middle (A) and vertex (B) region of a graphene sheet to the total emission current $I_0$ vs the local electric field strength calculated for a graphene sheet with a height, width, and thickness of 400, 1000, and 10 nm, respectively, and an inter-electrode distance of 0.1 mm.

Figure 37. Current–voltage characteristics of a graphene sheet from the experiment [24] (A, dots) and model calculation [23] (B, dashes) for a graphene fragment with the dimensions 400, 1000, and 10 nm in height, width, and thickness, respectively.

Figure 38. Distribution of the electrical field amplification factor (a) and the emission current density (b) along the edge of a graphene sheet calculated for the sheet with rectangular (lines 2, 4 and 6) and rounded vertices (lines 1, 3, 5) according to the expression $H = 500 – (x – a + 1.5)^2$. The parameter $a = 1.5, 2.5, \text{ and } 5 \text{ nm for the lines 2, 4 and 6, correspondingly.}$
The calculations and experiments performed imply that the structure of a graphene sheet causes an essential non-homogeneity in the distribution of the electrical field amplification factor along the list edge. Such a non-homogeneity is caused by the existence of sharp vertices in which vicinity the amplification factor has an abrupt maximum. One can try to change the structure of the graphene sheet in order to decrease the degree of non-homogeneity of the field amplification factor. The results of such a change obtained through the numerical calculations [23] are shown on figure 38. As is seen, rounding the vertices of the sheet can make the distribution of the electrical field amplification factor more homogeneous.

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