REVIEWS OF TOPICAL PROBLEMS

Contents

Graphene: fabrication methods and thermophysical properties

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<u>Abstract.</u> Current research on graphene, a 2D hexagonal structure of carbon atoms, is presented. The structural features of and basic methods for obtaining graphene are discussed. The phononic properties of graphene and their dependent graphene characteristics are examined. In particular, how to measure the thermal conductivity of graphene is discussed and recent experimental and theoretical advances on this subject are described. The stability problems of 2D crystal structures are addressed and the dimensional effects in the dependence of graphene characteristics on the lateral size are discussed. Simulation methods for determining the phononic characteristics and thermal conductivity of graphene are reviewed.

1. Introduction

Shortly after the present article was approved and accepted for publication in *Physics-Uspekhi*, the message came from Stockholm reporting that the Nobel Prize in Physics 2010 was awarded to two physicists, A K Geim and K S Novoselov, of Russian extraction, "for groundbreaking experiments regarding the two-dimensional material graphene." This

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Received 27 May 2010, revised 13 September 2010 Uspekhi Fizicheskikh Nauk **181** (3) 233–268 (2011) DOI: 10.3367/UFNr.0181.201103a.0233 Translated by A V Eletskii; edited by A Radzig news has confirmed once again the relevance of graphene research activity discussed in the present review and the important place of graphene among new objects of physics.

Graphene constitutes a single-layer 2D structure with a hexagonal honeycomb lattice containing carbon atoms in vertices of regular hexagons having the side length of 0.142 nm. Such a structure is an original constituent of crystalline graphite where such graphene planes are separated from each other by roughly 3.4 nm. The recent discovery of a comparatively simple approach to separating the individual graphene samples [1-4] has resulted in a drastic rise in interest in the production, investigation and practical use of graphene. This interest is caused mainly by the extraordinary physical and chemical properties of graphene, such as high electrical and thermal conductivity, the dependence of its electronic characteristics on the occurrence of added radicals of various natures on the graphene surface, controlled energy gap width, the quantum Hall effect, the extraordinarily high carrier mobility, high elasticity, and good electromechanical properties. The above-mentioned features are very attractive in terms of the possible applied usage of graphene as a base for new nanomaterials with improved mechanical, electrical, and thermophysical characteristics, and also as an element of nanoelectronic devices. Practical realization of these opportunities will become possible as a result of detailed studies of graphene characteristics and the development of reliable and relatively inexpensive methods of synthesizing such exotic structures. The present article contains a review of the work performed recently and directed at solving the above-listed problems.

It should be noted that the discovery of graphene has stimulated the interest of researchers, directing their efforts to the study of the electronic properties of this material [1–6]. In the short period since the discovery of graphene, the number of publications in the field has exceeded several thousand and continues to rise at an accelerated rate. A quite comprehensive review of these publications has been done by the authors of Ref. [7]. A later review containing, along with a description of the electronic properties, a short survey of synthesis methods of graphene and an analysis of prospects for its applied usage was presented by the authors of Ref. [108]. This allows us to avoid the detailed consideration of issues related to the electronic properties of graphene, referring the reader to the above reviews and the literature cited therein.

A fundamental physical problem arising with respect to the invention of production methods for isolated graphene relates to the question concerning the possibility of the existence of regular 2D crystalline structures. A rigorous thermodynamic analysis, including the summation of the fluctuation of atomic positions in such a structure [8-10], results in an inference about the instability of both 1D and 2D crystalline structures. This inference, confirmed by later studies [11, 12], at first glance contradicts the actuality of the existence of graphene. However, the above-mentioned inferences about the instability of 2D crystalline structures have been obtained by using a set of simplified assumptions, including, first, the harmonic approximation and assumption of the absolutely flat structure of the 2D crystal. It would appear that the rejection of at least one of these assumptions cancels the prohibition on the existence of stable 2D crystals. Particularly, this follows from the experimental results [13] demonstrating the tendency of a freely suspended graphene to form a wavy structure. Apparently, the above prohibition is inoperative in respect to such an imperfectly flat structure. The results of the above-cited experiment are in qualitative agreement with calculations [14] performed by the molecular dynamics method and also indicating a rippled surface of graphene. The influence of the anharmonicity on the thermodynamic stability of 2D crystalline membranes one atom thick has been considered in detail in Refs [15-17], concluding that taking into account the anharmonicity removes the prohibition against the existence of 2D crystals. It should be emphasized that this question has not yet been fully clarified to date and one can hope that the active experimental studies and ab initio calculations being performed in many laboratories will result in understanding the origin of stability of 2D crystals whose most prominent example is represented by graphene.

Among the many remarkable properties of graphene, one should note the extraordinarily high thermal conductivity of this material. Measurements [18] and comprehensive numerical calculations [19] imply that the thermal conductivity coefficient of graphene ranges between 3500 and 5500 W m⁻¹K⁻¹, which is the record value for all known materials. Graphene, whose thermal conduction has a phonon origin, presents a unique object for the investigation of this phenomenon, because the processes occurring in such miniature systems can be modelled from the first principles with a rather high accuracy. This offers an opportunity for the scientific solution to one of the paradoxes of solid-state physics, existing already from the 1930s. This paradox relates to the monotonically increasing dependence of the phonon thermal conductivity of a defectless crystal on its size, which is caused by the enhancement of phonon degrees of freedom as the crystal size increases. The discovery of graphene and the development of approaches to measuring its physical characteristics, including the thermal conductivity, in combination with an impetuous widening of calculation opportunities

for investigation of materials on the atomic level, allows one to establish by the example of graphene those factors constraining the thermal conduction of regular 2D structures.

One more problem related to the investigation into the thermal conduction of graphene concerns the dependence of this quantity on the number of graphene layers in the film. The thermal conductivity of an individual graphene exceeds by more than two times that for crystalline graphite ($\approx 2000 \text{ W m}^{-1} \text{ K}^{-1}$). This means that the thermal conductivity coefficient of a film consisting of a number of graphene layers should decrease as the number of layers increases. This is caused by the occurrence of an additional mechanism of phonon scattering, which is related to the interlayer interaction in the film. The experimental study of the character of the thermal conductivity dependence on the number of graphene layers [138] permits light to be shed on the mechanism of phonon propagation in a 2D medium.

In should be added that graphene possessing a record value of thermal conductivity is considered to be a base for the material necessary for the development of future nanoelectronics. The practical realization of the great potential of the applied usage of graphene is only possible as a result of the development of simple and quite inexpensive methods for production of this material with desirable characteristics and in macroscopic amounts. Over the several years since the discovery of the first approach to separating graphene based on the mechanical exfoliation of graphite layers [1-4], many research laboratories have addressed their efforts to the development of novel, more effective methods of graphene production. These efforts have resulted in the development of several new technological approaches to the separation and purification of graphene, whose significance falls outside the scope of a solution to the specific practical task. Advances in this direction have stimulated both the development of novel approaches to graphene production and the elaboration of measurement methods permitting one to control the procedure of growing this material and to keep watch on its parameters in the course of synthesis.

The foregoing permits one to consider the topic related to the production and investigation of the physical and chemical properties of graphene to be a new and interesting branch of chemical physics, representing basic and applied interest. The present review reflects the main trends in the advancement of this branch, which concern the investigation of the graphene structure, the development of methods for the production of this material, and the exploration of its physical and chemical properties, involving specifically mechanisms of heat transport in such structures.

2. Structural properties of graphene

2.1 Structure of a graphene boundary

Defectless graphene sheets of infinite size are indistinguishable from each other. Needless to say, the real graphene samples have a finite size and are distinct from each other not only in size but in the boundary structure as well. These distinctions exert a notable influence on the characteristics of graphene and, in particular, on its electronic and transport properties. The structure of the graphene boundary is occasionally characterized (by analogy with single-walled carbon nanotubes) by a chirality angle that is defined as the angle between the line of the graphene boundary and the line formed by neighboring hexagons standing on their apices.



Figure 1. Illustration of the types of chirality of a graphene sheet boundary and various graphene structures [21].

This property of graphene is illustrated by Fig. 1 [21], presenting fragments of graphene samples with various boundary structures. One can single out between these patterns the zig-zag and armchair structures for which the chirality angle equals 0° and 30°, respectively. Intermediate structures are also possible, for which the chirality angle is found between the above values. An individual graphene sample can possess boundaries of various structures, as shown in Fig. 1 on the right. The graphene boundary structure can be determined with the aid of Raman spectroscopy [21]. The boundary structure of graphene determines the anisotropy of its transport characteristics, which is caused by distinctions in the lattice constant for various directions.

2.2 Structural defects in graphene

It can hardly be expected that a graphene sample of quite a large size would have a perfect structure. Depending usually on the synthesis method, the conditions of preparation, the temperature, and other issues, the graphene surface contains structural defects influencing the mechanical, electronic and transport characteristics of the sample. Structural defects change the electronic and phononic spectra of graphene, and make up the scattering centers for phonons and electrons; therefore, their occurrence is reflected in the transport characteristics of the sample. The most important types of graphene structural defects are shown in Fig. 2. The vacancy defect corresponds to the lack of a carbon atom in the graphene hexagonal lattice. The Stone-Walls defect is a result of the substitution of a pentagon-heptagon pair for a pair of hexagons. The adsorbate defect is formed as a result of the attachment of an atom, radical, or functional group to the graphene surface. Since all the above-listed defects change, as a rule, the interatomic distance in the graphene hexagonal cell, the occurrence of defects usually results in a distortion of the graphene flat structure.

Along with the defects shown in Fig. 2, graphene samples may contain defects formed as a result of isotopic or chemical substitution of carbon atoms in the structure, as well as dislocation type defects manifesting themselves in the displacement of the fragments of a graphene layer with respect to each other. The occurrence of these defects also influences the transport characteristics of graphene.

2.3 Disruptions of a graphene flat structure

As mentioned above (see Introduction), flat 2D crystalline structures are not stable with respect to transverse vibrations [9-12]. The existence of stable graphene sheets is in contra-



Figure 2. Structural defects in a graphene sheet: (a) fragment of a graphene sheet with an attached OH radical; (b) Stone–Walls defect, and (c) vacancy defect.

diction with this conclusion, which can be explained by the wavy (but not perfectly flat) equilibrium structure of a graphene surface [13, 14]. This assumption is also confirmed by the results of a series of experiments performed recently, as well as by numerical simulations. These publications will be considered briefly below.

The authors of Ref. [13, 22] have presented conclusive experimental evidences for disruptions of the flat structure of graphene suspended between two supports. The graphene samples were produced by micromechanical exfoliation of crystalline graphite, which will be described in the forthcoming Section 3.1 of the present article. These samples were placed onto an SiO₂ film 300 nm thick covering the silicon substrate, and were characterized by means of an optical or scanning electron microscope (SEM). A metal grid consisting of Cr strips 3 nm in width and Au strips 100 nm wide spaced between 400 and 1000 nm apart was deposited by using electron beam lithography onto the surface of the film covered with graphene sheets. Then the region of the substrate covered with a graphene sheet was exposed to chemical etching, thus resulting in graphene sheets suspended on the metal grid. The samples containing the suspended graphene sheets several micrometers in size were studied by means of a transmission electron microscope (TEM). The number of layers in the samples of suspended graphene was determined on the basis of TEM observations at various orientation angles of the electron beam in relation to the graphene surface. The results of such measurements imply a deviation of the suspended graphene structure from a flat one, which manifests itself in a broadening of Bragg diffraction peaks observed at a fixed orientation angle. The treatment of the results of diffraction measurements indicates that the root-mean-square deviation of the orientation angle of the surface of a single-layer graphene from zero accounts for 5°, whereas for two-layer graphene this parameter accounts for $\sim 2^{\circ}$. The distortion of the graphene flat structure is observed for the size of the region exceeding 15 nm. According to measurements, the characteristic height of 'wrinkles' on the graphene surface amounts to about 1 nm.

This wavy structure of the graphene surface was also observed by the authors of Ref. [23], who used for this aim a SEM in combination with an atomic force microscope (AFM). Graphene samples between 0.5 and 20 μ m in width and between 0.35 and ~ 16 nm thick were bridged over a longitudinal trench in an Si/SiO₂ substrate. Figure 3 presents the typical measurement results obtained by means of an AFM. As is seen, the graphene surface contains wave-like longitudinal inhomogeneities oriented perpendicular to the direction of the longitudinal trench in the substrate. According to the measurements performed with 50 various samples, the characteristic wavelength of these inhomogeneities ranges between 0.37 and 5 μ m, and their amplitude falls within the range between 0.7 and 30 nm.



Figure 3. (a, b) The results of studying the structures of two graphene sheets suspended over a trench in an Si/SiO_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.

The measurements [23] revealed a temperature dependence of the amplitude and lateral size of inhomogeneities for the suspended graphene surface. Thus, heating a sample of suspended graphene up to 700 K results in either enhancement of the amplitude and wavelength of these inhomogeneities or wrinkling of the graphene surface. Wrinkling is accompanied by the sagging of several suspended graphene sheets to the bottom of the trenches. The above-described surface structure inhomogeneities of suspended graphene sheets disappear practically fully as a result of heating the sample up to approximately 450-600 K. When cooled to room temperature, these inhomogeneities, however, arise again with a much higher wrinkle amplitude than in the initial samples. Longitudinal and transversal wrinkles were observed on the graphene surface together with the sagging of the graphene toward the substrate trench. Such a behavior can be explained by a difference in the thermal expansion coefficient (TEC) of the substrate material (silicon) and graphene. The issue related to the TEC of graphene is considered in detail below.

It should be noted that, in accordance with the results of experiment [24], the difference in the values of TEC for graphene and the substrate material can be the only reason for the disruption of the graphene flat structure. The authors of Ref. [24] studied this phenomenon by the use of Raman spectroscopy combined with atomic force microscopy. Graphene samples between 0.5 and 20 µm in width ranging between 0.35 and 2 nm in thickness were produced by micromechanical exfoliation of graphite. These samples, consisting of one layer or a few layers, were bridged over a longitudinal trench in an Si/SiO2 substrate 3 µm in width. The samples were studied at atmospheric pressure and varied temperatures by means of a micro-Raman spectrometer with the resolution of 0.5 µm. In parallel with Raman spectral measurements, the suspended graphene sheets were studied by means of AFM. It was observed that the initial sample possesses a practically flat structure. A small shift of the Raman spectral peak, $\Delta \omega_{\rm G} = 25 \text{ cm}^{-1}$, between the suspended section of the graphene sheet and the region in contact with the substrate surface implies a mechanical stress experienced by the suspended fragment. A periodic variation of the temperature within the range between 300 and 700 K results in a further increase in the shift of the Raman peak position relating to the graphene region in contact with the substrate, while the position of the peak corresponding to the suspended graphene region remains unchanged. Moreover, wavy creases appear on the suspended graphene surface as a result of the periodic variation of temperature; they are up to 5.2 nm in height and possess an average wavelength of about

 0.26μ m. There is no doubt that such a behavior is caused by a distinction in the magnitudes of TEC for graphene and the substrate and, in particular, by a negative value of TEC for graphene.

The flat structure of graphene suspended over a trench in a substrate, found in the above-cited work [24], can hardly be considered to be a demonstration of the thermodynamic stability of such a structure, because graphene in this case is exposed to the action of the expansive force from the support and cannot be considered free.

2.4 Carbon 1D chains

The discovery of graphene has stimulated the fantasy of researchers who are looking for an opportunity to produce and investigate new carbon structures. A transition from 2D objects, to which a graphene sheet belongs, to 1D systems presenting an elongated chain of carbon atoms bound by the chemical bond seems to be a natural step on this road. Up to the present time, such objects have been studied only theoretically because neither an effective way to produce them nor quite reliable experimental approaches to the confirmation of such a synthesis have been found. This problem has been resolved only recently owing to an effective application of electron microscopy [25]. Graphene flakes containing from 4 up to 20 layers were utilized as an initial material. Such flakes present a side product of electrical arc synthesis of carbon nanotubes (CNTs). A diluted ethanol suspension of a bare handful of soot containing such flakes was ultrasonicated in order to separate graphene sheets from each other. A drop of the suspension was applied onto a carbon grid which was inserted into a TEM chamber for observations and manipulations. Graphene sheets found on the grid were irradiated with an electron beam between 80 and 120 keV in energy at a current density of about 100 A cm^{-2} , which resulted in a partial decomposition of the graphene 2D structure and the formation of narrow graphene nanoribbons (GNRs). To avoid the total decomposition of GNRs, their further treatment was performed at a reduced level of the electron beam current density (about 4 A cm^{-2}).

High-resolution TEM observations indicate that such an irradiation results in the formation of chains one or two carbon atoms in width. A detailed study of the formation dynamics of such chains under the action of electron beam irradiation, performed using TEM, implied that holes are formed at the first stage of the process on the graphene surface, which are separated by a neck about 1.7 nm in width corresponding to graphene ribbon 6-7 carbon atoms in width. Further electron beam irradiation is accompanied by a reduction in the ribbon width and results in some cases in the formation of carbon 1D chains. One such chain is 2.1 nm in length, which corresponds to 16 carbon atoms, and behaves like an elastic spring. The contact between the end of the chain and the edge of a neighboring graphene is unstable, so that the chain migrates along the graphene surface by discrete jumps whose length corresponds to the carbon interatomic distance. Such a chain withstands electron beam irradiation with an energy of 120 keV and electron current density of 4 A cm⁻² up to 100 h, which is followed by its destruction.

The quantum-chemistry calculations performed by using the density functional theory (DFT) point to a dependence of the bond length in such a chain on the coordinate. In particular, this dependence manifests itself in the structure shown in Fig. 4, which presents two graphene planes connected by a carbon chain. An increase in the bond length



Figure 4. Interatomic bond lengths (Å) for a structure consisting of two graphene planes connected by a graphene 1D chain, as evaluated by quantum-chemical calculations.

as the chain end is approached is the reason for the electron beam-stimulated destruction of the carbon chain beginning from the edge region, not from its central section. The structure presented in the picture can be considered to be an illustration of a possible usage of carbon 1D chains as connecting elements in nanocircuits containing graphene sheets.

2.5 Graphene oxide paper

One of the areas of practical use of graphene relates to the development and fabrication of graphene paper consisting of a number of graphene sheets. Graphene paper can contain a notable quantity of water (graphene oxide paper), depending on the preparation conditions. It is now known that graphene oxide paper consists of nondegraded graphite regions with incorporated sp³-hybridized carbon atoms containing hydro-xyl- and epoxy-functional groups on both the upper and lower surfaces of each sheet, and those of carbon atoms with sp²-hybridization containing carboxyl and carbonyl groups, mainly on the edges of the sheet.

There are many publications devoted to the study of the properties of both pure graphene [27, 28] (including multilayer systems [26, 29–32]) and graphene oxide [33–36]. Experiments performed by employing various approaches state that graphene oxide paper contains various numbers of C–OH triple groups, C–O–C ether groups, > C = C < double bonds, and enole and ketone groups. For example, NMR ¹³C spectral lines [37] indicate the occurrence of C–OH, C–O–C, and > C = C < groups in a bulk material (the content of water comprised about 8–15% at room temperature). The concentration of isolated double C=C bonds is apparently rather low and depends on the degree of oxidation of the graphene oxide paper, because they are easily oxidized.

The character of IR absorption spectra does not practically depend on the temperature within the range of 123– 473 K, while the intensity of a water line at 473 K decreases abruptly down to 1/20 of the initial level [37]. This implies the removal of water molecules, which is accompanied by a disruption of the graphene oxide paper structure. X-ray diffraction (XRD) studies [69] also show that the structure of graphene oxide paper becomes much less ordered as a result of high temperature treatment, including the removal of incorporated water molecules.

A structural model of graphene oxide paper was constructed in Ref. [62] based on NMR measurements. In accordance with this model, graphene oxide paper consists of aromatic 'islands' varying in size, which are not oxidized and separated from each other by aliphatic hexagon rings containing C–OH groups, as well as epoxy groups and double bonds. Such a model only indicates the possibility of the existence of chemical compound but not the spatial orientation of functional groups. Hydroxyl groups are oriented perpendicular to the graphite plane, whereas the space between planes also contains water molecules. Aromatic compounds, double bonds, and epoxy groups are arranged almost within the carbon network plane. Only carbon attached to OH groups forms a slightly distorted tetrahedral configuration that manifests itself in some layer deformation. Functional groups lie below and above the carbon network, thus forming a layer of oxygen atoms of a variable concentration.

Structural studies of graphene oxide paper were performed in Ref. [38] by the use of Raman spectroscopy and STM. The observed blue shift of the G-band in the Raman spectrum with respect to graphite (peak G corresponds to the E_{2g} mode of symmetric expansion–compression vibrations of sp² bonds) was explained qualitatively within the framework of DFT calculations in the plane-wave approximation. Comparison of measured and calculated spectra resulted in the conclusion that the shift is caused by the alternation of double and single carbon bonds in sp²-hybridized ribbons. Carbon atoms at the zig-zag boundary of the ribbon are therewith in the sp³-hybridization state (Fig. 5c).

Attachment of hydrogen atoms to each side of a clean graphene sheet results in the formation of graphane [39] (Fig. 5b) in which the hybridization of carbon atoms changes from sp^2 to sp^3 . This is accompanied by the removal of the conducting p-band and opening of the forbidden band, so that a semimetal with good conductivity transforms into an insulator [40]. TEM observations indicate that the graphane produced is transparent and holds its hexagonal structure. However, the lattice parameter in such a structure is about 5% shorter than that in graphene (2.46 Å). In this case, the compression of the lattice is rather inhomogeneous and the lattice parameter is not constant for various local parts of the membrane. The hydrogen addition reaction is reversible, so that the initial metal state of graphene, the lattice parameter, and even the quantum Hall effect can be recovered as a result of annealing.

DFT calculations [35] allowed the optimization of graphene oxide structures for various coverages of the surface with oxygen and hydroxyl groups. Concentrations of these radicals corresponding to the minimum of the total energy have also been obtained. The model developed describes rather readily available experimental results. In particular, it was revealed that 100% functionalization of graphene oxide paper is less advantageous in terms of energy than 75%. Moreover, it was shown that in the case of 25% coverage, the addition of both oxygen atoms and hydroxyl groups is more advantageous than the addition of only hydroxyl groups. The calculations also demonstrated that a reduction in the oxygen content (ratio C:O=16:1) of graphene oxide paper from 75% to 6.25% proceeds rela-



Figure 5. Schematic representation of the crystalline structure of graphene and its derivatives: (a) graphene; (b) graphane, and (c) a layer of graphene oxide paper after reduction.

tively easily, while the further reduction is rather hindered. The electrical properties of graphene oxide paper are determined by the coverage of the surface: for coverage exceeding 25% such a material is an insulator, whereas at less coverage it conducts electricity.

3. Graphene production methods

The experience gained in working with nanostructures demonstrates that the physical characteristics of such objects are very sensitive to both their production method and the specific conditions of the synthesis. Such a peculiarity is also significantly inherent to graphene. Namely, it manifests itself in a considerable spread (within 2–3 orders of magnitude) of the results of measuring the thermal conductivity coefficient for the samples synthesized in various conditions. In this connection, it seems appropriate to consider in detail the most widely used methods for the synthesis of graphene before presenting information related to the thermal conduction of this material. This provides the reader with a notion of the technical problems arising before the experimentalist dealing with nanometer-sized samples.

In the several years since the first publication on the production and investigation of individual graphene samples, so many various approaches to the synthesis of this material have been elaborated that one should be surprised why graphene had not been discovered many dozens of years before. This paradox can be resolved by taking into account that the most difficult stage of graphene synthesis is not so much the synthesis of samples themselves as identifying and establishing their main parameters (size, number of layers, etc.). As noted by the authors of the pioneering studies [1–4] reporting the first successful efforts to produce and observe individual graphene samples, this success became possible due to the fact that graphene placed onto an Si substrate covered with an SiO₂ layer of carefully fitted thickness is visible with the aid of an optical microscope. The interferometric picture formed is different from that of an empty substrate, which allows the identification of graphene by the comparison of microimages [2, 4]. In doing so, the requirement concerning the thickness of the oxide layer on the substrate is rather rigid-graphene becomes absolutely invisible when this parameter is changed by 5%. Further studies have shown that the reliable identification of graphene can be performed not only by optical microscopy but also Raman spectroscopy. The description of the approaches below to the production of graphene is accompanied by a detailed consideration of experimental procedures utilized when studying this material, taking into account the importance of experimental techniques and methods for the development of investigations in the graphene field.

3.1 Micromechanical exfoliation of graphite

Graphene samples were first separated through the micromechanical cleavage of graphite [1–4]. In accordance with this approach, 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 μ m in width and roughly 100 μ m in length having an ordered structure.

The main problem arising in the course of production of graphene sheets by this micromechanical method lies in the difficulty of their identification. The procedure of micromechanical separation of graphene sheets from crystalline graphite is similar to writing a text in pencil [4]. As this takes place, the micromechanical action on graphite results in the formation of a large number of fragments with various numbers of layers (from one to hundred). The proportion of single-layer graphene sheets in this conglomerate is relatively low, so that the main difficulty of the method under consideration consists in detection of such single-layer sheets. Standard methods of observation based on the employment of scanning probe microscopy are unsuitable for the identification of such systems because they do not permit the determination of the number of layers in a multilayer structure. The deciding factor that facilitated a considerable progress in the production and identification of single-layer graphene samples was the utilization of an optical microscope. Observations have shown [1-4] that a single-layer graphene sheet applied onto a silicon substrate covered with a thin SiO₂ layer gives rise to an interference image which furnishes definite evidence of the existence of graphene. The possibility of obtaining such a picture is very sensitive to both the thickness of the oxide layer and the purity of its surface. Thus, the use of a substrate with an oxide layer 315 nm instead of 300 nm thick resulted in a total disappearance of the interference picture. Notice that Raman spectroscopy has thereafter shown its worth as an effective means in the experimental study of graphene [21], allowing the determination of not only the number of layers in a graphene structure, but also the mutual arrangement of layers in it.

3.2 Liquid phase exfoliation of graphite

The simplest approach to the exfoliation of graphite into separate graphene sheets is based on the utilization of surfaceactive organic liquids. Such an approach is based on using a layered structure of graphite permitting the penetration of atoms or molecules of various kinds into the interlayer space of crystalline graphite [41]. This results in an enhancement of the interlayer distance and correspondingly in lowering the energy of interaction between them. As a consequence, the separation of graphite layers becomes possible under a mechanical action on them. It should be noted that this approach has manifested itself quite well in the resolution of the issue related to the separation of carbon nanotubes [42-46], which are usually produced in the form of closely packed bundles requiring further separation. In this case, N-polymethylpirrolidon (NMP) was used as a surface-active substance (SAS), being characterized by the high energy of interaction with the graphene layers.

Prolonged ultrasonication or/and centrifugation of finely disperse graphite in a surface-active liquid results in the formation of a suspension containing suspended singlelayer graphene sheets and few-layer graphene samples. Such a possibility is thermodynamically due to the higher energy of SAS interaction with the graphene sheet surface compared to that for interaction of neighboring sheets with one another. As a good example of the separation of graphene layers using an SAS, Ref. [47] can be mentioned, where a graphite powder sifted through a fine sieve was utilized as an initial material. A suspension of this powder in NMP was ultrasonicated, thus resulting in the formation of a homogeneous grey-colored liquid containing particles of a macroscopic size, visible to the naked eye. After removal of those particles by centrifugation, a homogeneous dark suspension is formed, which holds their properties for 5 months after preparation. Other SAS compounds, such as N,N-dimethylacetamide (DMA), g-buthyrolactone (GBL), and 1,3-dimethyl-2-imidasolidinon (DMEU), have also manifested themselves quite well in the separation of carbon nanotubes, being utilized as a SAS for the liquid phase exfoliation of graphene sheets.

Graphene sheets contained in those suspensions prepared by the above method were studied by means of a TEM. For this purpose, a suspension drop was deposited onto a hole in the carbon network. Observations imply the presence of three types of objects. First of all, there are flat single-layer graphene sheets. Curved graphene sheets were also observed. Finally, one could see two-layer and multilayer graphene samples. In all these cases, the lateral size of these objects reached several micrometers. Some graphene sheets tended to have bent or rolled-up edges.

The number of layers in the graphene samples produced was determined with the aid of a low-energy electron diffraction (LEED) method. In accordance with this approach, the information about the number of layers is contained in the ratio of intensities $I_{(1100)}/I_{(2110)}$ of diffraction peaks {1100} and {2110}. Statistical treatment of diffraction patterns for a large number of samples [22] has provided the distribution of graphene samples over the number of layers, represented in the form of a histogram. The bimodal shape of this distribution with the peaks at $I_{(1100)}/I_{(2110)} \sim 0.35$ and ~ 1.5 implies the occurrence of bilayer and single-layer graphene samples [22]. In this case, the proportion of singlelayer graphene sheets in the suspension comprises about 28%, which corresponds to a mass content of $\sim 12\%$ and to a total yield of single-layer graphene sheets (the ratio of the mass of single-layer graphene sheets to the total mass of the initial graphite powder) reaching $\sim 1\%$. The proper identification of single-layer graphene sheets is confirmed by matching the measured intensity ratios with the results of earlier measurements of $I_{(1100)}/I_{(2110)} \sim 0.4$ for bilayer and $I_{(1100)}/I_{(2110)} \sim 1.4$ for single-layer graphene sheets [22], and by Raman spectroscopy measurements.

Comparison of Raman spectra of graphene sheets with those of crystalline graphite implies that the procedure of separating graphene sheets does not notably distort their structure. The spectra do not contain any features indicating the occurrence of oxidized carbon atoms. A similar conclusion is also made on the basis of the results of sample investigation by the use of X-ray photoelectron spectroscopy and IR optical spectroscopy. However, X-ray photoelectron spectroscopy data point to the presence of some amount (about 10 wt.%) of residual SAS in samples. This admixture cannot be removed either by drying the sample at room temperature and a residual gas pressure of about 10^{-3} Torr or by vacuum annealing at 400°C. The electrical conductivity of the graphene films produced was determined at a level of $\sim 6500 \text{ S m}^{-1}$, which is close to that for graphene oxide, and the transparency was measured as amounting to about 42%.

One more approach to the issue of the liquid phase exfoliation of crystalline graphite was demonstrated by the authors of Ref. [68], who produced high-quality graphene sheets using (as an initial material) finely dispersed graphite powder that underwent a quick (1 min) thermal treatment at 1000 °C. Then, the mixture of the powder (10 mg) with microcrystalline NaCl was further ground, which resulted in

the formation of a gray powder. This powder was flooded with water and filtered, which allowed the separation of microcrystalline graphite. The filter deposit was treated with fuming sulphuric acid containing about 20% of free SO₃. After removal of the acid by filtration, the sample was inserted into a 40% water solution (130 ml) of tetrabutylaluminum hydroxide (TBA) containing 10 ml of N,N-dimethylformamide (DMF), and ultrasonicated for 5 min. The suspension obtained was kept at room temperature for 3 days in order for the TBA molecules to fully penetrate into the interlayer space of the graphite crystals. Next, 5 ml of this suspension was mixed with 15 mg of 1,2-distearoyl-sn-glycerol-3-phosphoethanolamine-N-[methoxy(polyethyleneglycol)-5000] (DSPE-mPEG) and was ultrasonicated for an hour, which resulted in the formation of a homogeneous suspension. A material containing predominantly single-layer graphene sheets was produced as a result of centrifugation of this suspension for 3 min. AFM study of this material deposited from the suspension onto a substrate has indicated that it contains about 90% single-layer graphene sheets of various sizes and structures. Processing the images obtained for hundreds of samples has allowed concluding that the average lateral size of graphene amounts to $\sim 250\,$ nm, and the average height over the substrate surface is about 1 nm. Single-layer graphene sheets were also studied by means of TEM and by the slow-electron diffraction method. Observations imply that the microimages of these objects are roughly similar to those observed recently for graphene samples produced by micromechanical graphite exfoliation [1-4].

Before making AFM observations of graphene samples, an SiO₂ substrate was moistened for 20 min in a graphite suspension, which was followed by water washing and drying in an Ar flow. Then, the substrate was calcinated at 350 °C and annealed at 800 °C in an H2 atmosphere. IR spectra were measured by means of a Fourier spectrometer. A transparent tablet containing a mixture of graphene sheets with microcrystalline KBr as a background was fabricated for this aim. TEM observations of graphene sheets were performed at an accelerating voltage of 120 kV. Samples were prepared by applying a drop of graphene suspension onto a carbon filament grid. X-ray photoelectron spectra (XPS) of the graphene samples were obtained with the use of the Al (K_{α}) line. The spot under irradiation was $150 \times 800 \ \mu m$ in size. The sample for XPS measurements was prepared by applying a drop of suspension onto a silicon substrate, followed by drying. The measured XPS spectra of graphene were compared with those of graphene oxide (GO) and highly oriented pyrolytic graphite (HOPG).

With the aim of measuring their electrical characteristics, the samples of graphene sheets and, for comparison, GO were applied onto an etched SiO₂/p⁺⁺-Si substrate 500 nm thick. The samples were calcinated at 350 °C and annealed in a hydrogen atmosphere at 800 °C, which was necessary to remove the surfactant. Then, Pd (20 nm) or Ti (1.5 nm)/Au(20 nm) pads were deposited onto the substrate using electron beam lithography; they secured the contact with the graphene layers. The samples were annealed in Ar for 15 min at 300 °C for the purpose of improving the contact. Langmuir–Blodget films were prepared on the basis of a standard approach, using the suspension of graphene sheets in DMF.

Appropriate measurements indicated that the typical electrical resistance of an individual graphene sheet 100 nm in width ranges between 10 and 30 k Ω . The resistances of

annealed and unannealed samples were found to be close to each other, while that of GO exceeded by hundreds of times the relevant magnitude for graphene. The temperature dependence of the graphene resistance within the temperature range between 50 and 300 K is a monotone decreasing function which can be fitted by a power law with the exponent -2.

3.3 Graphite oxidation

A very effective approach to the question of graphite layer exfoliation is based on the use of chemical oxidizers [48]. According to this approach, inner graphite layers are oxidized as a result of the action of strong gaseous oxidizers, primarily oxygen and halogens. This is accompanied by an increase in the interlayer distance in the crystal and, therefore, by a decrease in the interlayer interaction energy. This facilitates the possibility of liquid phase separation of graphene layers, which permits the synthesis of graphene oxide samples hundreds of micrometers in lateral size [49–53]. Subsequent reduction of graphene from oxide is also performed with the use of chemical action. Thus, GO sheets produced by the oxidation of graphite in an oxygen atmosphere can be reduced by means of chemicals utilizing such reducers as hydrogen and hydrazine.

The procedure of volumetric oxidation of graphite, accompanied with an enhancement of the interlayer distance in the crystal, has already been known since the middle of the 19th century [54–61]. The degree of oxidation, as well as the chemical composition of the oxides formed, are determined by the conditions of the oxidation process, the type of initial material (graphite), and the sort of reagents [37, 62-65]. Investigations have shown that the surface of the oxidized graphite layers usually contains hydroxyl and epoxy groups, while the edges of the sheets may be terminated with carbonyl and carboxyl groups. The structure of oxidized graphite is acted upon by the presence of water molecules, which promote an increase in the interlayer distance from the standard value of 0.34 nm to 1.2 nm [65]. The hydrophilic nature of graphite oxide layers provides an opportunity for their separation as a result of prolonged stirring or ultrasonication of a water suspension containing finely dispersed GO [66, 67].

The most widely used approach to the oxidation of graphite is based on the Hummers method [57] that consists in the utilization of an anhydrous mixture of concentrated sulfuric acid, sodium nitrate, and potassium permanganate. In accordance with the cited Ref. [57], 100 g of finely dispersed graphite powder and 50 g of sodium nitrate are introduced into 2.3 1 of sulfuric acid and stirred thoroughly at a temperature of 0 °C. Next, 300 g of potassium permanganate is slowly added to the suspension, simultaneously continuing stirring and keeping the temperature no higher than 20 °C. The oxidation reaction is then performed for 30 min at a temperature of 35 °C. The reaction proceeds accompanied by the growth in the volume of the mixture and bubbling. On completing the reaction, the suspension takes on a paste-like structure and grey-brown color. This paste is flooded with 4.6 l of water under stirring, which results in a rapid gas evolution and heating up to 98 °C. The brown suspension obtained is kept at this temperature for 15 min. Then, the suspension is flooded with 141 of warm water containing 3% hydrogen peroxide which promotes the reduction of the remains of the potassium permanganate and manganese oxide to a colorless soluble manganese sulphate. The

hydrogen peroxide treatment imparts a bright yellow color to the suspension. Filtration of the suspension leads to the formation of a yellow-brown paste. Repeated washing of this paste with a large amount of warm water permits the removal of practically all the admixtures and the formation of a pure graphite-oxide water suspension. Centrifugation followed by vacuum treatment at 40 °C in the presence of phosphoric anhydride (P₂O₅) promotes the removal of water from the suspension. The chemical composition of the graphite oxide produced was determined by combustion analysis. The measurements indicate that the material contains 47% carbon, 28% oxygen, and 23% water. There are also minor admixtures of ashes (at a level of 2%).

Graphene oxide layers contained in the water suspension possess a considerable negative charge which is caused by the attachment of cations present in water. This promotes the electrostatic repulsion of graphene layers in water, which facilitates their separation and enhances the suspension stability.

Based on the above features, the authors of Ref. [52] have demonstrated a relatively simple approach to extraction of oxidized graphene samples. Finely dispersed graphite oxide produced by the modified Hummers method [58-61, 68] was flooded with high-purity water, which resulted in the formation of a brown suspension. This suspension was then exposed to dialysis, promoting the total removal of the remains of salts and acids. The concentration of the suspension comprised 0.05 wt.%. Ultrasonication of the suspension for 30 min resulted in the separation of graphite oxide into GO sheets. Then, the suspension was centrifugated for 30 min with 3000 cpm (the rotor radius measured 14 cm) in order to remove graphite oxide particles which had not been subjected to exfoliation. Subsequent reduction of graphene from GO was performed as a result of mixing 5 ml of the suspension with 5 ml of water, 5 ml of a 35% water solution of hydrazine, and 35 ml of a 28% water solution of ammonium in an ampoule. The mass ratio of hydrazine to GO reached 7:10. After thorough stirring for several minutes, the ampoule was placed into a water bath, where it was kept at $\sim 95 \,^{\circ}\text{C}$ for an hour. The suspension produced contained graphene sheets and was used further for investigation and preparation of a film. The remains of hydrazine were removed through dialysis upon completing the reduction procedure. The graphene paper was fabricated by filtration of the suspension using a filter 47 mm in diameter with a pore size of 0.2 µm.

The graphene sheets obtained filling the suspension were studied by UV and visible spectroscopy in both the absorption and transmission modes. The average size of the graphene sheets was monitored during the reduction by means of a particle analyzer. The reflection spectra of graphene films were measured using the Fourier IR spectroscopy method. Images of the graphene sheets were obtained by means of an AFM operating in the tapping mode. The electrical conductivity of the films was measured by the four-probe method at an intercontact distance of about 1 mm. Mechanical tests on the films were performed at an initial loading of 0.001 N and the rate of its increase of 0.01% min⁻¹.

Investigations indicate a high responsivity of the suspension stability to the residual admixtures of metal salts and acids frequently occurring in initial graphite oxide. These admixtures can neutralize the charge of graphene layers, thus resulting in worse stability. Ammonium may be added to the initial reaction solution, which raises the pH value to 10 and increases the charge density on the graphene sheets. Volatile ammonium is easily removed from graphene samples during the formation of films or composites. A surplus content of hydrazine also promotes the raising of pH; however, its use is limited due to the toxicity. It was ascertained that the graphene layers occurring at the water/air interface tend to agglomerate, which results in the formation of visible black particles on the suspension surface. This problem can be effectively resolved by adding a layer of water–immiscible

eliminate the air/water interface. The process of graphene reduction with the aid of hydrazine was monitored by UV and visible absorption spectroscopy. The measurements indicate that the GO absorption peak at $\lambda = 231$ nm is shifted gradually to red in the course of the reaction, reaching $\lambda = 270$ nm at completion of the reaction, about an hour after beginning. The abovedescribed approach to producing the graphene suspension offers a simple way for separation of individual graphene samples destined for study. In doing so, it is sufficient to apply a drop of the suspension onto a substrate and remove the liquid fraction by drying. As distinct from GO paper, graphene paper cannot be redispersed through ultrasonication in water, which points to its water-repellent property.

liquid (such as mineral oil) to the solution in order to

The above approach to obtaining a water suspension containing graphene sheets was utilized thereafter by the authors of Ref. [69] for preparation of a dense material based on graphene (graphene paper). For this purpose, the suspension was passed through a membrane filter 47 mm in diameter with a pore size of 0.2 μ m, which was followed by peeling from the filter and drying in air. The thickness of the graphene paper could change from several dozen nanometers to 10 μ m, depending on the volume of the suspension to be filtered. The typical thickness of the samples under investigation came to 6 μ m. Paper samples were annealed for an hour either in air at a temperature below 220 °C or in argon at a temperature above 220 °C. GO paper fabricated in the same manner was used for comparison.

The thermal properties of the graphene paper were studied by means of thermogravimetric analysis (TGA). According to this approach, the sample under investigation is placed onto an analytic balance in the thermostat and is exposed to a dosed flow of air or oxygen. The temperature of the thermostat is gradually increased, thus resulting in a partial oxidation of the sample and loss in its weight due to the liberation of volatile products. The interrelation between the temperature and the rate of the weight loss allows one to arrive at a conclusion about the thermal stability of the material. The measurements were performed either in flowing air or (for comparison) in flowing nitrogen (40 ml min⁻¹) within the temperature range of 30–800 °C with a ramp rate of $5 \,^{\circ}$ C min⁻¹. At the same time, the graphene paper samples were studied by the X-ray diffraction method at room temperature. The samples were cut with a razor into rectangular strips approximately 4×15 mm in size for mechanical testing. The electrical conductivity of the samples was measured by the four-probe method. Microimages of the graphene paper were obtained by means of an SEM.

Thermogravimetry investigations into the properties of graphene paper [49] point to its high thermal stability. A little loss in weight at temperatures below 200 °C is assigned to the evaporation of water molecules. The loss in weight within the temperature range between 200 and 500 °C relates to decomposition of the remains of oxygen-containing groups.

The TGA characteristics of graphene paper do not contain a sharp kink at 200 °C, as distinct from the graphene oxide (GO) paper. This implies the absence of most of the oxygencontaining groups that have been removed through hydrazine reduction. The total mass loss of graphene paper within the temperature range between 200 and 500 °C does not exceed 10%, which is considerably lower than that for GO paper (about 30%). Thermal treatment of graphene paper within the temperature range between 200 and 500 °C does not result in either a change in its visual appearance (shiny smooth surface) or a breakage of its integrity. This is a useful advantage of graphene paper over GO paper, which notably folds upon heating above 200 °C due to strong gas evolution as the result of thermal decomposition [70]. Therefore, graphene paper possesses much higher thermal stability than GO paper.

The results of X-ray diffraction analysis [49] imply that the annealing of graphene paper promotes a microstructural ordering of samples. Thus, the interlayer spacing in an unannealed sample accounts for 0.387 nm, which exceeds that in crystalline graphite by more than 10%. As the annealing temperature increases, the interlayer spacing decreases, reaching the value of 0.341 nm at 500 °C, which is close to that for crystalline graphite. A decreasing dependence of the interlayer spacing in graphene paper on the annealing temperature is caused by the thermal removal of added radicals of oxygen, hydroxyl (OH), and carbonyl (CO), whose occurrence promotes an increase in the interlayer spacing in graphene paper.

Measurements [49] indicate that the electrical conductivity of graphene paper produced as a result of the thermal decomposition of GO is lower than that for graphene paper produced by the above-described method. This is due to structural disruptions of graphene layers, occurring in the removal of added radicals as a result of thermal treatment. Thus, the electrical conductivity of GO paper treated at 220 and 500 °C accounts for 0.8 and 59 S cm⁻¹, respectively, while that of graphene paper annealed at the same temperatures is equal to 118 and 351 S cm⁻¹, respectively. The electrical conductivity of a graphene paper sample annealed at 500 °C exceeds by an order of magnitude that for a finely dispersed, pressed graphite powder, which implies a strong interaction between layers in the graphene paper.

The results of the investigations performed point to good mechanical properties of graphene paper, which are caused by a high degree of layer ordering. The measured values of stiffness and tensile strength of graphene paper do not differ notably from those of GO paper [66]. These characteristics rise as the annealing temperature increases, reaching 41.8 GPa for the Young modulus and 293.3 MPa for the breaking stress at a temperature of 220 °C. These values are notably lower than those for individual graphene layers, which may be linked to a relatively weak interlayer interaction; they considerably exceed, however, the relevant characteristics of GO paper and are more than 10 times as much as the magnitudes for a flexible graphite film [66]. Thermal treating of graphene paper at a temperature exceeding 220 °C makes it fragile, and the measured values of its stiffness and breaking stress show decreasing annealing-temperature dependences.

The above approach to the reduction of graphene from GO based on the usage of hydrazine has been modified by the authors of Ref. [71], who at a preliminary stage of the process treated the sample with sodium boron hydride and an aryl-

diazonium salt of sulphanilic acid. By doing so, the graphene sheets became water-soluble and repel one another in the solution due to a negative charge inherent to the added SO₃ radical. A finely dispersed, powdered GO produced from polycrystalline graphite by means of the Hummers method (see above) was utilized as an initial sample. The procedure of graphene reduction included three stages: (1) treatment of GO samples with sodium boron hydride at 80 °C for an hour, resulting in the removal of the most oxygen-containing groups; (2) sulphonation of the sample by aryl-diazonium salt of sulphanilic acid in an ice bath for 2 h, and (3) hydrazine treatment at 100 °C for 24 h, resulting in the removal of the remains of oxygen-containing groups. The graphene sheets exposed to sulphonation easily form a homogeneous suspension in water with a concentration of up to 2 mg ml^{-1} , having a pH between 3 and 10. Isolated graphene layers are also retained in water-diluted organic solvents, such as methanol, acetone, and acetonitrile. The preliminary reduction of graphene at stage (1) is necessary for both reduction as fully as possible at stage (3) and enlargement of a fraction of the graphene sample surface containing sp² carbon and accessible for the sulphonation reaction at stage (2). Elemental analysis reveals that the sample exposed to the preliminary reduction at stage (1) is sulphonated up to the ratio S: C = 1:35, while in the absence of stage (1) the sulphonation results in the ratio S: C = 1: 148. The elemental analysis also implies the presence of nitrogen at a level of 3% in the final product.

The addition of a larger amount of sodium boron nitride into the sulphonated suspension promotes an immediate precipitation of graphene flakes from the solution, while inserting hydrazine at stage (3) does not result in the precipitation of the deposit, even after keeping it at $100 \,^{\circ}$ C for 2 days.

In contrast to Refs [52, 66], where the hydrazine treatment of GO in water brought about irreversible coagulation and precipitation of graphene sheets, in the experiment under consideration [71] the water suspension containing sulphonated graphene kept its stability for 24 h, even after hydrazine treatment. This is caused by the presence of negatively charged SO_3^- on the graphene sheet surface, thus promoting an electrostatic repulsion of the sheets during the reduction process.

The degree of graphene reduction in proportion as the reaction proceeds was determined by means of NMR spectroscopy. The NMR spectra of GO contain two peaks: one at 134 ppm, corresponding to unoxidized sp^2 carbon, and the other at 60 ppm, corresponding to the epoxy group. Furthermore, there exists a shoulder at 70 ppm that corresponds to carbon with an added hydroxyl group. At a low degree of oxidation, the last two peaks overlap, and a weak broad resonance at 167 ppm is observable, corresponding to carbon atoms with an added carbonyl group. The peak at 60 ppm disappears as a result of the 1st stage of reduction, while the peaks at 70 ppm and 167 ppm are notably weakened. The peak at 134 ppm is shifted toward 123 ppm due to a change in the chemical environment of sp² carbon atoms. The final stage of reduction leads to the formation of weakly sulphonated graphene not containing resonances at 70 ppm and 167 ppm. A small peak at 140 ppm, which is not observable in the GO spectrum, may be ascribed to those carbon atoms with covalently added phenyl-SO₃H groups. The above-described kinetics of graphene reduction have been confirmed qualitatively by measuring the IR spectra of the samples at each stage of the process.

Table 1. Electrical conductivity of graphene and related materials [71].

Material	Graphene oxide	Sulphonated graphene oxide	Graphene	Graphite
Electrical conductivity, S m ⁻¹	0	17	1250	6120

AFM observations indicate a single-layer structure of GO and graphene samples contained in suspensions. According to the experimental evidence, the lateral size of GO sheets ranges between one and ten microns at a thickness of about 1 nm. Too prolonged an ultrasonication of the GO suspension promotes a decrease in the lateral sizes of the sheets, as well as a deterioration of their surfaces, which here are covered with small cracks. TEM images of individual graphene sheets show that they are bent at the edges. Microimages of water-soluble graphene sheets are practically indistinguishable from those for graphene samples produced by micromechanical cleavage of graphite [1–4].

Table 1 compares the measured values of the electrical conductivity of GO, sulphonated GO, and graphene samples with that of crystalline graphite. GO films about 3 µm thick applied onto a glass substrate were used in the measurements. The films were dried before taking the measurements in order to remove remaining moisture. According to the experiment, the GO conductivity is practically zero, which is caused by the absence of free electrons. The first stage of graphene reduction promotes an increase in conductivity up to 17 S m^{-1} , thus indicating the occurrence of a some number of free electrons. Further hydrazine reduction of the sample up to pure graphene is accompanied by roughly a 70-fold increase in the conductivity up to 1250 S m⁻¹. This value approaches the conductivity of crystalline graphite (6120 S m⁻¹). The difference in conductivities of a graphene film and graphite is seemingly caused by the limited sizes of the graphene sheets composing the film. In such a situation, imperfection of contacts between the neighboring graphene sheets can cause a decrease in the conductivity of the sample.

An alternative approach to the problem of graphene reduction from GO has been developed by the authors of Ref. [72], who reported a detailed study of the structure and chemical composition of GO sheets synthesized by the Hummers method. A finely dispersed graphite powder was utilized as an initial material. A sample of graphite oxidized by means of the modified Hummers method [57, 60] and purified was kept over phosphoric anhydride (P_2O_5) for a week in order to remove any remaining water. Dried GO samples were flooded with deionized water in the ratio 1 g l^{-1} , which resulted in the formation of a colloid solution. Then 5% sodium bicarbonate was added to the solution, which promoted an increase in its pH to 9-10. 100 g of the suspension obtained was flooded with 800 g of sodium boron nitride and stirred at 80 °C for an hour. This resulted in the formation of partly reduced graphene sheets that were washed repeatedly in a large volume of water to remove the residual ions. Then, the sheets were kept again in a vacuum chamber over phosphoric anhydride for two days. A dry sample of partly reduced graphene was thereafter flooded with highly concentrated sulphuric acid and stirred at 120 °C for 12 h. The powder produced was exposed to filtration and repeated water washing, which promoted the removal of most of the admixtures. The powder was pressed into a pellet several hundred microns thick and about 1.1 g cm⁻³ in



Figure 6. Schematic representation of the reduction procedure for graphene oxide [72]. The structure and measured electrical conductivity of the samples are shown at each stage of the process.

density. The pellet was annealed at a temperature of 1100 $^{\circ}$ C for 15 min in flowing Ar with an addition of 15 vol.% H₂. Graphene samples were studied before and after reduction procedure by means of the X-ray diffraction method, IR-Fourier spectroscopy, Raman spectroscopy, AFM, NMR spectroscopy, and X-ray photoelectron spectroscopy. Furthermore, the graphene samples were subjected to elemental analysis.

Results of ¹³C NMR spectroscopy studies indicate the occurrence of some quantity of 2-hydroxynaphthalic and 1,3-dihydroxyxanthone groups added to five- and six-member rings on the periphery of GO sheets. At the same time, five- and six-member rings with added lactol groups also make some contribution to the NMR signal.

The chemical composition of the samples was analyzed on the basis of treatment of the NMR spectra and X-ray photoelectron spectra at each stage of the reduction procedure, which permits one to get a notion on the mechanism of the process. The analysis implies that the reduction process contains two stages, which are illustrated in Fig. 6. Here, the oxidized graphene sheets are marked GO, and the graphene samples at different stages of reduction are symbolized as CCG1, CCG2, and CCG3. The first stage of the reduction process consists in removal of oxygen and some oxygencontaining radicals as a result of the reaction with NaBH₄. This is evidenced by the NMR spectra of the sample CCG1 that barely contain features related to the presence of epoxy groups, alcohols, ethers, and ketones. The sample CCG1 by its appearance is much closer to graphite than to its precursor GO; its conductivity is 200 times higher than GO. The second stage consists in the reaction of the sample with highconcentration sulphuric acid, promoting the removal of hydrogen-containing radicals. Therefore, the CCG2 sample only contains sp²-hybridized carbon and a some number of carbonyl groups that manifest themselves in cross-polarization NMR spectra. TEM observations reveal a tendency of individual CCG2 graphene sheets to aggregate, resulting in the formation of larger flakes between 200 nm and 2 μ m in size. However, single-layer graphene sheets are also observable on the periphery of these flakes.

Subsequent thermal treatment of the CCG2 sample in flowing Ar/H_2 at a temperature of 1100 °C for 15 min results in a twelvefold increase in electrical conductivity to a level of 2×10^4 S m⁻¹ inherent to crystalline graphite. This is also accompanied by the disappearance of the NMR ¹³C signal

from the CCG3 sample spectrum. Annealing makes the sample like pure graphite. The above two-stage approach to graphene production is advantageous compared to both the procedure based on the employment of hydrazine and the procedure of graphene thermal reduction, since in this case the products of reduction contain a minimum number of functional groups and possess higher electrical conductivity. Furthermore, this approach does not require the use of such highly toxic compounds as hydrazine or dimethylhydrazine.

The results of electrical measurements performed at each stage of graphene reduction permit the monitoring of changes in the electronic structure of the sample during the reduction. The initial GO sample is an insulator with conductivity at a level of 0.5 S m⁻¹. The above-described reduction procedure results in enhancement of the conductivity by about 4 orders of magnitude, which points to the effective restoration of a π -conjugated structure. A control test wherein NaBH₄ treatment was not applied, so that the sample was treated by only high-concentration sulphuric acid, resulted in an increase in the conductivity just to a level of 46.4 S m⁻¹.

C1s X-ray photoelectron spectra (XPS) of samples recorded at each stage of graphene production also indicate the effective restoration of C-C bonds as a result of treatment and the occurrence of a small number of carbonyl groups at the last stage. The XPS signal of the initial GO sample contains a double peak, which implies a high percentage of oxidized carbon atoms. The spectra taken from the samples of reduced graphene contain a single peak with a small feature in the high-energy range, which evidences the prevalence of C-C bonds. A small feature in the spectrum of the CCG2 sample near 288.5 eV corresponds to added ketone and carboxyl groups. A peak at 291 eV is observable for both the CCG3 sample and graphite, thus indicating that delocalized π conjunction is conserved in the samples. In compliance with data determined on the basis of processing XPS spectra and chemical analysis, the CCG3 samples contain insignificant quantities of sulfur ($\sim 0.5 \text{ wt.\%}$) and nitrogen (0.5 wt.%). Thus, the graphene samples produced differ from those synthesized earlier by the use of hydrazine [52, 71] (nitrogen content reaches 3.25% and sulfur content comes to 2.8%). The oxygen content in the CCG2 sample was measured as 12.7 wt.%, which corresponds to the results of measurements taken in Refs [52, 71] for the same samples. Annealing lowers the oxygen content in the CCG3 sample to 0.5 wt.%, which is inherent to finely dispersed graphite. Notice for comparison that the direct thermal treatment of GO samples in an Ar atmosphere at a temperature of $1050 \,^{\circ}$ C preserves the oxygen content at a level of 9.3 wt.% [73].

CCG3 samples have the capability to form a stable suspension not only in water but also in dimethylformamide (DMF). Such a suspension exposed to ultrasonication for 50 min remains stable for at least several weeks. Whereas the solubility of GO in deionized water exceeds that in DMF, chemically reduced graphene sheets demonstrate higher solubility in DMF than in water, which relates to their hydrophobic nature. Therein lies the distinction of graphene samples produced in Ref. [72] from those synthesized previously [52, 71], the latters showing higher water solubility than DMF solubility.

3.4 Synthesis of graphene by chemical vapor deposition (CVD) method

The method of chemical vapor deposition (CVD) is widely used for the synthesis of carbon nanostructures. Thus, beginning in the early 1970s, this method has been effectively utilized for the fabrication of carbon fibers comprising the base of a composite material with extraordinary mechanical characteristics [74]. The CVD method is one of the most widespread approaches to large-scale production of carbon nanotubes [75]. This approach is based on the possibility of thermal catalytic decomposition of gaseous hydrocarbons on the surface of some metals with the formation of various nanocarbon structures. As an example of a successful application of the CVD method to the synthesis of graphene can be mentioned Ref. [76], where an Ni film less than 300 nm thick was utilized as a substrate playing the role of catalyst. This film was applied onto an SiO_2/Si substrate by means of electron beam deposition. The graphene synthesis was performed in a quartz tube through which a CH₄: H₂: Ar mixture flowed at a ratio of 50:65:200 and a temperature of 1000 °C. On completing the synthesis reaction, the samples were cooled at the rate of $\sim 10 \,^{\circ}\text{C} \, \text{s}^{-1}$ to room temperature under an argon flow. The experience has shown that such rapid cooling is an important factor preventing the agglomeration of graphene sheets into multilayer structures and promoting separation of those sheets from the substrate for further utilization.

The resulting SEM images contain distinguishable graphene samples having various numbers of layers. The thickness of the film can also be estimated by means of a TEM. In order to perform optical studies and Raman spectroscopy measurements, the film was transferred onto a silicon substrate covered with a SiO₂ layer 300 nm thick. The observations indicate that the average number of graphene layers and the degree of coverage of the substrate are determined by the thickness of an Ni film and the duration of the growth process. Thus, a film synthesized for 7 min on an Ni substrate 300 nm thick typically contained bilayer graphene samples. The analysis of AFM images testifies to a wavy structure of the graphene sheet surface. While the authors of Ref. [76] ascribed this phenomenon to a difference in the thermal expansion coefficients of Ni and graphene, such a structure can be caused by the instability of the purely 2D crystalline graphene structure considered above.

The Ni substrate may be removed by using an aqueous solution of ferric chloride (FeCl₃) (1 M), which permits the selection of individual graphene samples. This allowed etching the substrate without extra gas evolution or deposit precipitation. After several minutes of such etching, the

graphene film was easily separated from the substrate and came to the surface of the solution. The remains of the Ni film were removed using diluted hydrofluoric acid after transfer of the film onto the substrate.

Along with the above approach to transferring graphene sheets onto a substrate by the use of acid etching, a method based on the utilization of a soft substrate, such as a polymethylsiloxane (PDMS) stamp, was also developed in Ref. [76]. According to this method, a PDMS stamp is pressed first on a graphene film grown on an Ni substrate. After removal of the Ni substrate by means of FeCl₃ etching, the graphene film turns out to be attached to the PDMS substrate. By varying the shape of the Ni substrate, one obtains graphene films of various sizes and shapes that can be transferred onto an arbitrary substrate.

The optical and electrical characteristics of the graphene films produced were measured by means of a spectrometer and four-probe measurement device, respectively. For measuring the transmission spectra in the visible and UV ranges, film samples 1×1 cm in size were applied onto a quartz substrate. The measurements showed that the transmission coefficient of a film grown for 7 min on an Ni substrate 300 nm thick amounted to about 80%. For performing electrical measurements, indium contacts were applied onto each angle of a quadratic film 1×1 cm in size. The measured resistance of the film amounted to $\sim 280 \Omega$. As the duration of the treatment of the film by ozone and UV-irradiation increases, the resistance also grows, which relates to a decrease in the number of layers as a result of the treatment.

Graphene film samples were transferred onto a doped silicon plate covered with an oxide layer 300 nm thick for the purpose of measuring the carrier mobilities. The localization of individual single-layer graphene samples was easily determined by the optical contrast and Raman spectra. Multicontact electrical measurements yielded the electron mobility of 3750 cm² V⁻¹ s⁻¹ at the number density of carriers equal to $\sim 5 \times 10^{12}$ cm⁻².

Results of the measurements performed imply that the graphene films possess electromechanical properties. This follows from the measured dependences of the resistance of the film applied onto a flexible polymer substrate on the bending radius. The experiment demonstrates a repeatedly reversible increase in the film electrical resistance as the curvature radius characterizing bending decreases, which points to the possibility of using graphene in nanoelectronics as a base for a nanoelectromechanical device that transforms a mechanical signal into an electrical one, and vice versa. The simplest example of such a device is a telephone transforming sound vibrations of air into electromagnetic oscillations. The maximum bending at which the restoration of the initial electrical resistance of the film is possible after removal of the mechanical load corresponds to a curvature radius of 0.8 µm at a relative tension of 18.7%. More significant bending is often accompanied by mechanical damage and decomposition of the graphene film.

Subsequent efforts addressed at improving the CVD method of graphene sheet production have resulted in a considerable enlargement of the size of samples synthesized, which makes this method the best one compared to various other approaches to solving this problem. Thus, Ref. [81] reports on the fabrication of samples of a single-layer graphene about 1 cm in lateral size. This result exceeds by tens of times those reached previously and gives optimism in respect to the prospects of using graphene in nanoelectronics.

The graphene samples were grown by the CVD method on a copper foil 25 µm thick in flowing methane and hydrogen at a temperature of 1000 °C. The graphene film grown measuring 1×1 cm in area was studied by the use of optical, transmission, and scanning electron microscopes, as well as a Raman spectrometer. Processing the measurement results indicates that the film generally has a uniform structure and contains largely single-layer graphene sheets with small inclusions of two- and three-layer flakes. Estimations performed on the basis of Raman spectral measurements point to the fraction of the area filled with single-layer graphenes exceeding 95%. The contribution of bilayer graphene sheets is estimated as 3-4%, so that the fraction of graphene flakes with the number of layers in excess of two does not exceed 1%. Studies have shown that graphene growth is a self-limiting process terminating within 10 min after the onset of synthesis. Therefore, the growth of graphene does not really occur if the substrate is covered with a single-layer graphene film. This implies a catalytic mechanism of the growth, for the realization of which the presence of a copper surface is important.

The electrical characteristics of the graphene films produced were studied in a configuration of a field-effect transistor, where Al_2O_3 was utilized as a gate. The measured value of the carrier mobility came to approximately 4050 cm² V⁻¹ s⁻¹, and the number density of carriers at the Dirac point was equal to $n_0 = 3.2 \times 10^{11}$ cm⁻². These values are an order of magnitude lower than those for graphene samples produced through the mechanical cleavage of graphite; however, one may expect that a further modification of the above-described growth method will result in the improvement of these parameters.

The optimistic expectations are supported by the results of more recent experiment [82], the authors of which have managed to enlarge the size of a graphene sheet up to 75 cm diagonally. This achievement permits one to assume that the method under consideration can become a basis for industrial production of graphene sheets of macroscopic size with the goal of developing flexible conducting transparent films for utilization in notebook monitors, mobile phones, and other 'touch screen' devices. Graphene sheets were synthesized on the basis of the CVD method in a cylindrical chamber 20 cm in diameter. A copper foil sheet 75 cm diagonally rolled into a cylinder was used as a substrate. A quartz tube 18.75 cm in diameter was inserted inside the foil cylinder, which provided a homogeneous temperature distribution over the substrate surface. At the first stage of the process, the sample was blown for 30 min with hydrogen at a temperature of 1000 °C and a pressure of 90 mTorr at the rate of 8 cm³ min⁻¹. This resulted in enlargement of the grain size in the copper foil structure from several μm to ~ 100 μm . The graphene synthesis was performed at the same temperature for 30 min by passing a CH₄/H₂ mixture through a chamber at the rate of 32 cm³ min⁻¹ at a ratio of 3:1 and total pressure of 460 mTorr. On completing this procedure, the sample was rapidly cooled in flowing hydrogen (at a rate of $10 \,^{\circ}\text{C s}^{-1}$) to room temperature, at a hydrogen pressure of 90 mTorr. The subsequent procedure of separation of the graphene sheet from the copper substrate consisted of several stages. First and foremost, the graphene sheet grown on a copper film was attached to a polymer film by applying soft pressing $(\sim 2 \text{ MPa})$ between two rollers. Then, the copper film underwent electrochemical etching by means of a water solution (0.1 M) of ammonium persulphate $[(NH_4)_2S_2O_8]$,

which resulted in the formation of a transparent conducting graphene film on the polymer substrate. After removing the remains of copper by using deionized water, the graphene film could be transferred from the polymer substrate onto any other surface. For this purpose, the film was rolled between rollers at a velocity of 150–200 mm min⁻¹ at an elevated temperature (90–120 °C) together with the desired substrate. This led to the formation of a flexible transparent film whose electrical properties were determined by the characteristics of graphene. Repeating the above-described procedure allows the production of multilayer graphene sheets with enhanced conductivity. Polyethylene terephthalate (PET) was used as a substrate for such films.

Raman spectroscopy measurements reveal that the graphene films produced largely possess single-layer structure. However, some isolated islands of two-layer and even multilayer graphene are also visible on microphotographs obtained by means of AFM and TEM. The analysis of Raman spectra implies that each of the individual layers conserves its properties during subsequent formation of graphene films from single-layer sheets, so that the mutual orientation of hexagonal planes corresponding to various layers is arbitrary, in contrast to crystalline graphite. Graphene film samples were held for 5 min in a water solution (63%) of HNO₃ in order to impact their electronic characteristics. Such p-doping resulted in a shift of G peak in the Raman spectrum by 18 cm⁻¹, which was accompanied by splitting this shifted peak in the region of localization of twolayer graphene islands. This implies the different degrees of doping for upper and lower graphene layers.

Measurements have shown that a graphene film applied onto a polymethylmetacrilate (PMMA) substrate have a transparency of 97.4% and an electrical resistance of 125 $\Omega \Box^{-1}$. A p-doped four-layer graphene sheet possesses a transparency of about 90% and a resistance of about 30 $\Omega \Box^{-1}$, which roughly corresponds to an inversely proportional dependence of the resistance on the number of layers. The carrier mobility determined by the Hall measurements accounted for 7350 cm² V⁻¹ s⁻¹ at a temperature of 6 K.

3.5 Electric arc graphene production

Experiments show that an electric arc with graphite electrodes, burning in an inert gas atmosphere, is one of the most effective tools for the transformation of crystalline graphite into carbon surface structures. This approach has led to the development of methods for large-scale production of fullerenes [77] and carbon nanotubes [78, 79], which has provided researchers with easy access to these structures. For this reason, one could expect that the electric arc method would turn out to be useful for graphene production, as well. This idea has been recently realized by the authors of Ref. [80], who have used for this aim a discharge in hydrogen.

The samples of GO prepared by the above-described Hummers method [57] were utilized as the initial material for the graphene production. Typically, 0.5 g of finely dispersed graphite powder and 0.5 g of NaNO₃ were mixed with 23 ml of concentrated sulphuric acid at a temperature of 0° C. Then, 3 g of KMnO₄ was slowly added to the suspension obtained while stirring and maintaining a low temperature. Forty-six ml of distilled water was added to the suspension after 12 h of continuous stirring, which was followed by stirring the aqueous suspension for 15 min. After that, the suspension was exposed to a 140-ml flow of warm water (40–50 °C) and 10 ml of a 30% solution of hydrogen peroxide. Finally,

the suspension formed was filtered, rinsed with deionized water, and dried in a vacuum oven for 24 h at 60 °C. This procedure resulted in the formation of GO, which was treated in a DC electric arc in a hydrogen-argon mixture at a ratio of H_2 : Ar = 1 : 9 at atmospheric pressure. A graphite rod 10 mm in diameter and 150 mm in length was used as a cathode, and a rotating graphite cylinder having 8 holes 20 mm in diameter and 10 mm in depth filled with an oxidized graphite powder was employed as an anode. The interelectrode spacing was maintained at 2 mm, and the discharge current ranged between 100 and 150 A. The arc discharge treatment resulted in the reduction of graphene from GO. Ten mg of the material fabricated containing graphene was exposed to a 10-ml flow of N-methylpirolidone, and the suspension obtained was ultrasonicated for 2 h and then centrifugated. This promoted the removal of large graphite particles and aggregates. The dispersion formed as a result of centrifugation was filtered and dried in a vacuum at a temperature of 60 °C for 24 h.

For comparison, samples were synthesized by using all the above-described procedures, except that a discharge in pure argon was utilized in one case instead of the discharge in an H₂–Ar mixture, and some samples were synthesized in another case by applying thermal treatment in an Ar atmosphere at 1050 °C instead of gas discharge processing.

The samples fabricated were studied by the X-ray diffraction method (XRD), X-ray photoelectron spectroscopy, IR Fourier spectroscopy, Raman spectroscopy, thermogravimetry within the temperature range between 30 and 1000°C, nitrogen cryosorption, scanning electron spectroscopy (SEM, electron energy of 15 keV), transmission electron spectroscopy (TEM, electron energy of 200 keV), and atomic force microscopy (AFM). The samples for TEM observations were prepared by applying a drop of graphene suspension onto a copper grid, followed by drying. The samples for AFM observations were applied onto an SiO₂/Si substrate 300 nm in width. The electrical conductivity of the graphene sheets was measured by means of a scanning tunnel microscope (STM) equipped with a piezomanipulator. These measurements were performed using gold contacts at an applied voltage ranging between -2.5 and +2.5 V.

An analysis of XRD measurements indicates that the graphite oxidation promotes an increase in the interlayer spacing from 0.335 to 0.83 nm. Ignition of an arc causes a fast increase in the temperature of the sample (the temperature rises above 2000 °C in less than 20 s). This promotes the thermal detachment of the oxygen-containing groups added to the inner graphite layers, which is accompanied by an abrupt elevation of the inner pressure capable of overcoming the van der Waals attraction of graphene layers. The shape of the diffraction pattern implies a considerable disordering of layers in the sample. An analysis of SEM images of graphene sheets points to their rippled structure with a set of pleats. The measured value of the specific surface area $(570 \text{ m}^2 \text{ g}^{-1})$ of the samples is considerably lower than that for an individual graphene layer ($\sim 3000 \text{ m}^2 \text{ g}^{-1}$). Hence follows the presence of a large number of multilayer graphene structures or graphene sheets with partially overlapped surfaces.

Subsequent separation of graphene layers is performed by the use of standard methods with the application of centrifugation and ultrasonication. This results in the formation of a homogeneous suspension mainly containing singlelayer graphene sheets. TEM observations show that the majority of graphene samples contain a small number of bends. In this respect, the samples synthesized differ from those produced as a result of thermal exfoliation of graphite [83–85], which contain a large number of bends and other distortions of the flat structure. These features are well seen in TEM images at a moderate magnification. AFM studies also give evidence of a high quality of the electric arc-produced samples. According to these studies, the characteristic height of graphene sheets placed on a substrate ranges between 0.9 and 1.1 nm, thus indicating their single-layer structure. This conclusion is also confirmed by the measured Raman spectra containing a feature at about 2644 cm⁻¹, which is inherent to single-layer graphene structures produced by both the micromechanical exfoliation of graphite [86, 87] and the chemical reduction of GO [49].

The coefficient of graphite transformation into singlelayer graphene sheets by electric arc synthesis is estimated at a level of about 18% (by weight). The number of residual oxygen-containing functional groups in graphene sheets was evaluated by the XPS method. Similar measurements were performed, for comparison, with initial graphene samples and those produced by using the thermal exfoliation of graphite, as well as with samples prepared by the exfoliation of graphite in an argon discharge. The measurements demonstrate that C1s XPS spectra of graphene sheets produced in a hydrogen arc discharge do not contain the feature related to the C = Ogroup. Therefore, these spectra are very similar to those of the initial graphite material. The results of the elemental chemical analysis imply that the graphene samples synthesized hold 6-7% of oxygen. For comparison, this content for graphene samples prepared by exfoliation of graphite in an argon discharge amounts to 8.5%; for the graphene samples produced by applying the thermal exfoliation of graphite, it reaches 10%; for the graphene samples produced as a result of the thermal exfoliation of graphite followed by hydrogen treatment, it equals 6.5% [88], and for the graphene samples chemically reduced from GO by means of hydrazine, it equals 10% [70]. The graphene samples synthesized in Refs [38, 73] from GO by thermal reducing contain 5-10% oxygen.

The conclusion about a low content of oxygen in the graphene samples produced by the electric arc method in hydrogen is confirmed by the analysis of IR spectra. These spectra exhibit a rather weak feature at 1730 cm⁻¹, which corresponds to the longitudinal C = O vibration. This feature is more pronounced in the samples synthesized in an argon electric arc discharge and the thermal exfoliation of graphite, thus indicating a higher content of oxygen groups.

Raman spectroscopy has also been used for comparison of graphene samples synthesized by different methods. The Raman spectra of all the samples exhibit clearly pronounced features at ~ 1330 and ~ 1590 cm⁻¹, which correspond to the known D and G bands inherent to graphite. The intensity ratio of those bands (I_D/I_G) is the measure of disordering of graphene layers. This ratio measured for graphene samples synthesized in the electric arc turned out considerably lower than that for the samples produced by thermal exfoliation of graphite. At the same time, the intensity ratio measured for the samples produced in a hydrogen arc discharge is notably lower than that for an argon discharge.

One more informative approach to studying the quality of graphene sheets is based on the application of TGA (see Section 3.3). Comparison of TGA data for the graphene samples produced by different methods demonstrates that the samples synthesized in an electric arc in the presence of hydrogen show the highest thermal stability with respect to oxygen. The characteristic temperature of thermal

decomposition of these samples (601 °C) exceeds that for both the samples produced by thermal exfoliation of graphite (507 °C) and the samples synthesized in an argon electric arc (525 °C). This is due to the more perfect structure of the samples synthesized in the hydrogen electric arc and by the absence in them of added oxygen-containing groups that are removed in the discharge forming H₂O molecules.

The electrical characteristics of graphene sheets were measured by the authors of Ref. [79] inside a TEM chamber with the employment of a standard approach utilizing an STM tungsten tip as a probe. The measurements show that the electrical conductivity of a sample synthesized in a hydrogen electric arc $(2 \times 10^3 \text{ S cm}^{-1})$ considerably exceeds that for both the sample produced in an argon arc discharge $(2 \times 10^2 \text{ S cm}^{-1})$ and the sample synthesized by the thermal exfoliation of graphite (~ 80 S cm⁻¹). The higher electrical conductivity of the samples synthesized in the hydrogen arc discharge also points to the structural perfection of these objects compared to the samples synthesized by other methods.

3.6 Thermal decomposition of silicon carbide

One more effective approach to the synthesis of graphene is based on the thermal decomposition of silicon carbide, resulting in the epitaxial growth of a graphene film on the surface of an SiC crystal [4, 89–92]. The main advantage of such an approach is the size of the sample synthesized, which can be comparable to that of an SiC crystal, providing its quality is quite good. Moreover, the electrical characteristics of a graphene sheet can be measured, if it is applied onto a dielectric substrate. Since SiC crystal constitutes a dielectric, in this case such measurements do not meet with technical problems related to the necessity of transferring a sample from a metal to a dielectric substrate.

Results of the first experiments concerning the synthesis of graphene through the thermal decomposition of SiC [90-95] indicate a high sensitivity of the quality of the samples synthesized to the degree of perfection of the initial crystal. The lateral sizes of these samples did not exceed several hundred nanometers, which is related to the polycrystalline structure of the initial crystals involved. Furthermore, the film grown in the above-cited experiments was inhomogeneous over the surface, as follows from electron microscopic observations. A notable improvement in the degree of homogeneity of graphene films grown by the thermal decomposition of SiC has been reached by the authors of Ref. [92] by virtue of a thorough treatment of the crystal surface. 6H-SiC(0001) wafers having a high degree of orientation were utilized as the initial material. In some experiments, substrates doped with nitrogen at a concentration of $(1-2) \times 10^{18}$ cm⁻³ were used. Before the thermal treatment procedure resulting in the formation of graphene film, the samples were etched for 15 min by hydrogen at atmospheric pressure and the temperature $T = 1550 \,^{\circ}\text{C}$, which promoted the removal of the remains of the grinder from the surface. Graphene was synthesized in a vertically oriented water-cooled double-wall quartz tube in slow flowing argon. The temperature was raised to the nominal value at a rate of 2-3°C per second; on completing the synthesis procedure, the chamber was cooled at the same rate to the initial temperature. The synthesis was performed either under vacuum conditions or at an argon pressure ranging between 10 and 900 mbar; the duration of the synthesis was typically 15 min, and the temperature of the synthesis ranged between 1500 and 2000 °C.

The chemical composition of the surface and the thickness of the graphene films were determined by the X-ray photoelectron spectroscopy method at a photon energy of 700 eV and with a resolution of ~ 350 meV. At the same time, the films were also studied by the use of the angle-resolved photoelectron spectroscopy (ARPES) method (photon energy of 94 eV, total resolution of 25 meV, and sample temperature of 20 K). Measurements indicated that the oxygen content in the graphene films synthesized did not exceed 1%, even after holding in air for 1 h. However, more prolonged air conditioning was accompanied by the formation of adsorbed hydrocarbon and water layers on the graphene surface. These layers could be removed by vacuum thermal treatment at 600 °C. The morphology of the graphene film surfaces was studied by means of an AFM operated in the contactless mode. The structure of the films was studied by the low-energy electron diffraction (LEED) method, which yields a spatial resolution of better than 10 nm. The Raman spectra of the samples were measured using laser radiation at a wavelength of 532 nm. A spatial resolution of about 2 µm was provided by the utilization of a confocal optical resonator.

The electrical characteristics of the graphene films produced were measured with the use of Ti/Au pads as contacts that were thermally deposited onto a substrate. The films utilized for four-probe measurements were $100 \times 100 \ \mu m$ in size. The Hall measurements were performed with a graphene film $4 \times 50 \ \mu m$ in size in a magnetic field of $\sim 0.66 \ T$. The sample temperature ranged between 27 and 300 K.

AFM and TEM observations give evidence that the hydrogen etching causes the formation of flat, highly homogeneous longitudinal terraces between 300 and 700 nm in width on the initial surface of a 6H-SiC(0001) wafer. The direction and the width of the terraces are determined by the random orientation of the substrate with reference to the crystallographic (0001) plane. The characteristic height of the terraces is 1.5 nm, which corresponds to the dimension of the 6H-SiC unit cell in the direction perpendicular to the substrate surface. The length of the terraces can exceed 50 µm. The vacuum thermal treatment performed in the course of the graphene synthesis results in a notable change of the substrate surface: holes of up to 10 nm in depth form on it, whereas the initial terraces become hardly discriminable. The graphene films grown on such an in-homogeneous surface are also nonuniform in depth: regions covered with single-walled graphene films several hundred nanometers in size coexist with those filled with two-layer and few-layer graphene structures, as well as with islands that do not contain graphene at all.

Thermal treatment of SiC in an argon atmosphere (900 mbar) permits one to grow graphene films with improved morphology of the surface, in contrast to vacuum conditions of the synthesis, which do not provide a high quality of graphene. Terraces exceeding the initial ones by 5-8 times in size are discriminable in AFM images of such films. The height of the terraces is also enhanced and amounts to 8-15 nm on average. Larger-sized steps (exceeding 50 µm) that are nonuniform over the surface are also visible on the substrate surface along with the terraces. The better quality and larger lateral size of graphene samples synthesized in an argon atmosphere than those produced in vacuum conditions are due to the possibility of performing the synthesis in an argon atmosphere at a considerably higher temperature

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Table 2. The carrier mobility measured in graphene samples synthesized by the thermal decomposition of SiC in vacuum conditions and in an argon atmosphere [92].

Method of	Aethod of Method ynthesis of measurement	Mobility, $cm^2 V^{-1} s^{-1}$; temperature, K		
synthesis		300	K 27 1850 2000	
Annealing in argon atmosphere	Hall effect	900	1850	
	Four-probe method	930	2000	
Vacuum annealing	Hall effect	470	_	
	Four-probe method	550	710	

 $(1500 \,^{\circ}\text{C}$ instead of $1200 \,^{\circ}\text{C}$ in vacuum conditions). The use of elevated temperatures promotes graphene synthesis with a higher surface homogeneity because the increase in temperature is accompanied by an exponential growth in the diffusion rate of defects, and therefore offers an opportunity for the self-healing of the defects.

High-resolution low-energy electron microscope observations allow conclusions that the above steps are covered with flat homogeneous single-walled graphene ribbons. The characteristic size of these ribbons exceeds by many times that for the samples synthesized by means of vacuum annealing. Apparently, the size of the ribbons is only limited by the size of the steps on an SiC substrate. Two- and even three-layer graphene sheets are visible on the edges of the terrace steps, along with single-walled graphene structures. Therefore, one can conclude that the formation of new graphene layers begins from the edge regions on the substrate surface.

Low-energy electron diffraction microscope images point to an orientation of the graphene layer with respect to the crystallographic direction of the substrate plane at an angle of 30°. The XPS C1s spectrum of graphene differs from that of carbon entering into the composition of an SiC substrate. This demonstrates that graphene is not bound to the initial substrate through a chemical bond.

Table 2 presents the results of measuring the carrier mobility in graphene. It is seen that the carrier mobility notably decreases as the temperature increases, being weakly dependent on both the size of the sample and the measurement method. The Hall measurements yield the value of $\approx 10^{13} \mbox{ cm}^{-2}$ for the surface number density of carriers, which is in agreement with the measurements performed by the angle-resolved photoelectron spectroscopy (ARPES) method. This value of the carrier number density is comparable to the measurement data [3, 96] reporting the magnitude of 5×10^{12} cm⁻² for graphene samples produced by mechanical exfoliation of graphite and applied onto a highly doped SiO₂ surface. However, the carrier mobility $(10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ measured in the cited Refs [3, 96] exceeds notably that given in Table 2. It should be noted that the carrier mobility reported in Table 2 agrees well with the measurements by other authors [90, 97], who synthesized graphene by the thermal decomposition of SiC. The mechanism of epitaxial growth of graphene as a result of the thermal decomposition of SiC is considered in detail in Ref. [98].

3.7 Epitaxial growth of graphene on a metal surface

In parallel with SiC single crystals, metal surfaces with a wellordered crystalline structure are also used successfully as a substrate for the epitaxial growth of graphene [99–105]. A



Figure 7. Illustration of the mechanism of the epitaxial growth of graphene sheets on a Ru(0001) surface: (a) measured (upper line) and calculated (lower line) electron diffractograms of a Ru(0001) crystal; (b) measured and calculated diffractograms of a Ru surface covered with a single-layer graphene sheet, and (c) the same for a Ru surface covered with a two-layer graphene sheet. The relevant structures are shown on the right.

good example of such an approach is given by Ref. [99], where the ruthenium surface Ru (0001) was utilized as a substrate. The synthesis of graphene was performed in high-vacuum conditions and was monitored *in situ* by the LEED method. This permitted both observation of the formation of singlelayer graphene sheets and the fixation of the second-layer origin.

The layer-by-layer growth of large-sized graphene sheets on the Ru(0001) surface is based on an increasing temperature dependence of the carbon solubility in transition metals. The growth mechanism is illustrated in Fig. 7, which presents also the measured and calculated electronic diffractograms related to various stages of graphene growth. At high temperatures (about 1150 °C), the carbon solubility is quite high, so the metal sample is saturated with carbon over the entire volume. Slow cooling of the sample to $\sim 825 \,^{\circ}\text{C}$ results in about a sixfold decrease in the solubility [105], which causes the release of extra carbon on the metal surface. The surface is covered with large-sized (larger than 100 µm) film islands which are visible in SEM images. Electron microscope observations give evidence that this film represents singlelayer epitaxial graphene sheets having a moiré structure [100]. It should be noted that a similar moiré structure is also inherent to the graphene samples produced as a result of the epitaxial growth on the iridium surface Ir(111) [103, 104]. The size of the graphene sheets (larger than 100 µm) exceeds significantly those reached using epitaxial growth on a 4H-SiC(0001) surface (less than 1 µm) [95], Ru(0001) (about 1 µm) [101], and Ir(111) (about 1 µm) [104]. Diffraction measurements revealed the orientation of the graphene layers, which coincides with the (1010) direction in the substrate. The characteristic wavelength of the moiré structure amounts to 2.93 nm, which exceeds by about 11 times the spacing between nearest neighbors in a Ru(0001) crystal. Measurements also indicate a notably lower value of the electron work function of graphene compared to that for both the initial ruthenium crystal and the graphite material. This indicates the occurrence of electronic interaction between the substrate and graphene, which is caused by the charge transfer from the metal to the graphene sheet. A similar effect also follows from the results of simulations [106] performed for graphene sheets grown on an SiC surface.

The spatial structure of the graphene layers deposited on a ruthenium surface was studied by the use of Raman spectroscope providing high spatial resolution (400 nm). The spectra were excited by a focused laser beam at $\lambda = 532$ nm, and power on the level of 1 mW. Graphene surface maps 25×25 µm in size were obtained as a result of the measurements.

The transport characteristics of the graphene samples were measured by means of a standard four-probe scheme using tungsten tip contacts oriented at an angle of 45° relative to the sample surface and moved by application of piezoelectric manipulators. The transport characteristics of twolayer graphene sheets were measured utilizing two different configurations of the probes: either each of the layers is in contact with two probes or all the probes are in contact with the first layer. These measurements were combined with the field emission SEM observations. The measurement data demonstrate a notable distinction in the electrical resistances of graphene and the contact between the neighboring graphene layers. Thus, the resistance of a site of the first graphene layer 10 μ m in size was measured as 10 Ω , while the resistance of a contact between neighboring layers was about 1000 times higher. The mechanism of interlayer conduction was studied on the basis of measurements of the dependence of the interlayer contact resistance on the spacing between the layers, which could be controlled by applying a mechanical load drawing together the neighboring layers. The exponential character of the dependence measured gives evidence that the main mechanism of interlayer conduction relates to the tunneling of electrons belonging to a π orbital. The height of the relevant potential barrier was estimated on the basis of this dependence as 5 eV.

The interlayer spacing in two-layer graphene samples, as well as the distance between the graphene layer and the substrate, was determined by the LEED method. According to measurements, the first graphene layer is offset by 1.45 Å from the ruthenium substrate, while the distance between the first and second layers in a two-layer graphene equals 3.0 Å. The above distance between the ruthenium substrate and the first graphene layer is comparable to that (1.65 Å) measured for graphene sheets grown on a 4H-SiC(0001) substrate [107].

The observations demonstrate that the characteristic size of single-layer graphene sheets forming on a ruthenium surface as a result of cooling the sample amounts to about 200 µm, which corresponds to the typical distance between the centers of condensation. When the lateral size of singlelayer graphene sheets reaches about 100 µm, an intense formation of the second layer occurs on the surface of these structures. Both single-layer and two-layer graphene sheets are visible therewith on the surface. The first layer is bound covalently with the ruthenium surface, which is caused by hybridization of an electron belonging to a carbon $2p_z$ orbital with d electrons of ruthenium, whose energy corresponds to the Fermi level. This electron transfer process is not so important for the second graphene layer, and therefore the distance between the first and the second layers is primarily determined by the van der Waals mechanism, with the interlayer distance approaching the 3.34 Å inherent to crystalline graphite. For this reason, the addition of the second layer does not really change the distance between the first layer and the metal substrate (1.45 Å), and, therefore, it does not affect the character of the graphene-metal interaction.

4. Phonon properties of graphene

4.1 Phonon spectrum of graphene

The thermophysical characteristics of graphene (thermal capacity, thermal conductivity, thermal expansion coefficient) are determined by phonons. Features in the phonon spectrum of graphene and graphene-based materials relate to the 2D structure of a graphene sheet. Graphene possesses a hexagonal structure with two carbon atoms in each cell, which causes the occurrence of six phonon branches in the dispersion spectrum: three optical (LO, TO, ZO) and three acoustical (LA, TA, ZA). The phonon LA and TA modes correspond to longitudinal and transverse vibrations of carbon atoms in the graphene plane. The ZA mode corresponds to carbon atom vibrations in the direction perpendicular to those of LA and TA modes, i.e., in the direction normal to the graphene plane. At present, there are numerous measured and calculated data concerned with phonon dispersion for graphite and graphene (see Refs [19, 31] and references cited therein). According to these data, the LA and TA modes possess a linear dispersion, and the corresponding values of the speed of sound are $v(LA) = 21.3 \text{ km s}^{-1}$ and $v(TA) = 13.6 \text{ km s}^{-1}$ [19]. The character of dispersion of the ZA mode near the center of the Brillouin zone still remains unclear. Some authors report on the quadratic character of the ZA mode dispersion at the point Γ (see, for example, Ref. [109]), whereas calculated results [110] demonstrate linear dispersion at the speed of sound $v(TA) = 1.6 \text{ km s}^{-1}$.

The dispersion relation for phonons can be derived from the first principles on the basis of comprehensive calculations. In so doing, the ground state of the system in question is evaluated by the use of the density functional theory (DFT) [111, 112], while the linear response to a perturbation related to ion displacements is studied by means of the density functional perturbation theory (DFPT) [113–115]. The phonon spectra of graphene and related materials were calculated applying DFPT in Refs [31, 32, 116, 117].

The phonon spectrum of a material is principally determined by the force constant matrix expressing the second derivative of the energy E of the system with respect to the ion displacement u:

$$C_{\alpha i,\,\beta j}(\mathbf{R}-\mathbf{R}')=\frac{\partial^2 E}{\partial u_{\alpha i}(\mathbf{R})\,\partial u_{\beta j}(\mathbf{R}')}\,,\tag{1}$$

where **R** and **R**' are the Bravais lattice vectors, *i* and *j* label *i*th and *j*th atoms of the elementary cell, respectively, and α and β denote the directions of the coordinate axes. The dynamic matrix of the system may be expressed through the known force constant matrix:

$$D_{\alpha i,\beta j}(\mathbf{q}) = \frac{1}{\sqrt{M_i M_j}} \sum_{\mathbf{R}} C_{\alpha i,\beta j}(\mathbf{R}) \exp\left(-\mathrm{i}\mathbf{q}\,\mathbf{R}\right), \qquad (2)$$

where M_i is the mass of the *i*th atom. Then, the phonon frequencies at any point **q** of the Brillouin zone are the



Figure 8. Dependence of the graphene phonon frequencies on the number of neighboring lattice nodes included in the calculations of the force constant matrix for different phonon modes: solid line $-G_{LO/TO}$ mode; dash-and-dot line $-K_{TO}$ mode; dashed line $-M_{ZO}$ mode, and dotted line -ZA mode, $\frac{1}{4}$ path in the G-M direction [32]

solutions of the eigenvalue problem:

$$\omega^{2}(\mathbf{q}) u_{\alpha i}(\mathbf{q}) = \sum_{\beta j} u_{\beta j}(\mathbf{q}) D_{\alpha i, \beta j}(\mathbf{q}) .$$
(3)

The force constant matrix describes the interaction of perturbations in different nodes of the host lattice; in this regard, the interaction decreases as the distance between lattice nodes increases. In practical calculations of phonon spectra it is necessary to limit the number of interacting nodes in the lattice by a finite magnitude. Figure 8 displays a calculated dependence of the phonon frequency of graphene on the number of neighboring lattice nodes, included in the calculations of the force constant matrix for various modes [32]. As is seen, the calculated result notably depends on the number of neighboring lattice modes taken into consideration. The minimum number of nearest shells related to the neighboring lattice nodes that is necessary to include in the calculation for obtaining the result that is practically independent of this parameter is 4 for the phonon $G_{LO/TO}$, K_{TO} , and M_{ZO} modes. However, the convergence of the ZA mode in the number of neighboring nodes is considerably slower, and it is necessary to take into consideration at least 13 shells to yield a result independent of the number of neighboring lattice nodes. Calculations based on an empirical parameterization of the force constant matrix for graphene usually take into consideration 3–5 nearest neighbors [109, 118], and the relevant approximation parameters are evaluated as a result of their fitting to experimental data for graphite or calculated dispersion curves for graphene.

The results of DFT calculations of the phonon dispersion spectra slightly deviate from the experimental data obtained before 2007. In particular, the experimental data [119] obtained on the basis of the electron energy loss spectroscopy (EELS) provide higher frequencies for the TA branch in the direction G–M, and predict crossing of the TA and ZO branches between the points G and M, while the results of all the calculations indicate that these branches cross near the point M with a small shift towards the point K [32, 38, 120]. Moreover, EELS data [121, 122] predict the occurrence of a gap between ZO and ZA modes at the point K, whereas the calculations imply the crossing of these modes (Fig. 9a).

Figure 9b presents the dispersion of acoustic phonon branches measured by means of inelastic X-ray scattering for the whole region G-K-M-G [123] in comparison with the data obtained earlier by the use of the same method [105] and with calculated results [122]. As may be seen, the experimental data [123] agree much better with DFT calculations.

High-frequency optical modes TO and LO are degenerate at the point G, thus belonging to the E_{2g} representation. These modes have the characteristic frequency near $\approx 1580 \text{ cm}^{-1}$ and are used in Raman spectroscopy studies of graphene and related materials. Results of such studies have been reviewed in detail in Ref. [21].

Modes describing the relative vibrations of graphene layers appear in multilayer graphene structures. In the simplest case of a two-layer graphene, a new low-frequency ZO' mode occurs in the vibrational spectra, having a frequency of about 100 cm⁻¹ at the G point and correspond-



Figure 9. Phonon dispersion curves in graphene: (a) [32]: calculations by the generalized gradient approximation method (GGA, solid lines) and local density approximation method (LDA, dashed lines); measurements by the EELS method—squares, diamonds, and black dots; measurements by the neutron scattering method—white dots, and measurements by X-ray scattering—triangles. (b) [123]: calculations by DFT approximation method—solid lines; measurements by the inelastic X-ray scattering method—circles, triangles. Inset shows the first Brillouin zone and directions connecting the high-symmetry points G, M, and K.



Figure 10. Dependences of the frequency of low-frequency modes on the number of the graphene layers [116].

ing to optical vibrations of two layers in the direction perpendicular to the graphene plane. A low-frequency optical TO' vibration of layers along the plane at the frequency of about 40 cm⁻¹ also manifests itself. Furthermore, other optical phonon modes experience slight splitting (by about 5 cm⁻¹) [38]. The dependence of the frequency of low-frequency modes on the number of graphene layers was studied theoretically in Ref. [116] (see Fig. 10). It has been shown that the frequencies of interlayer optical vibrations increase as the number of layers rises, reaching maximum magnitudes when the number of layers is about 7.

The anharmonic character of lattice vibrations exerts some action on the phonon properties of graphene at finite temperatures. One of the most important characteristics of the anharmonic properties of graphene is the Grüneisen parameter, reflecting the dependence of the phonon frequency on the lattice cell size:

$$\gamma(\mathbf{q}, j) = \frac{-a_0}{2\omega_{\mathbf{q}, j}^0} \frac{\partial \omega_{\mathbf{q}, j}}{\partial a} \bigg|_0, \qquad (4)$$

where *a* is the size of the graphene unit cell, **q** is the vector of the Brillouin zone, *j* is the index of the phonon mode, and the index 0 corresponds to the equilibrium parameters of the lattice structure. The Grüneisen parameter can be evaluated on the basis of the calculated phonon dispersion with some deviation from an equilibrium lattice parameter. Generally, the Grüneisen parameter is positive due to an enhancement of the average lattice parameter and a decrease in the vibrational



Figure 11. Grüneisen parameters calculated for a single-layer (a) and twolayer (b) graphene [117].

frequency as the vibration amplitude increases. Under some conditions, however, the Grüneisen parameter for layered crystals can be negative [124].

The magnitudes of the Grüneisen parameter calculated for all the phonon modes of single-layer and two-layer graphene are shown in Fig. 11 [117]. As follows from the plots, the Grüneisen parameter for some graphene modes is negative. The highest negative values of the Grüneisen parameter correspond to the acoustical transverse phonon mode ZA. The frequency of this mode rises as the lattice parameter increases, because the tension of a graphene layer constrains the movement of atoms in the perpendicular direction (similarly to the behavior of a string that vibrates with a higher frequency and a lower amplitude under tension). This phenomenon was predicted by I M Lifshits in 1952 and is named as the 'membrane effect' [125].

One more parameter describing the interaction of phonons with one another and with other quasiparticles is the linewidth of the optical phonons. The width at half maximum for the Raman mode E_{2g} was measured as 13 cm⁻¹ [126]. *Ab initio* calculations [127] indicate that the linewidth of the E_{2g} mode and its temperature dependence are mainly determined by the electron–phonon interaction.

4.2 Lattice properties of graphene at a finite temperature

The behavior of the graphene lattice at finite temperatures exhibits some peculiarities which reflect the 2D nature of this material. First of all, one should note the possibility of the existence of 2D structures in itself. For 2D crystalline systems, as proven by Peierls and Landau [8-10], the magnitude of long-wavelength fluctuations of atoms within the plane diverges logarithmically in the harmonic approximation. Mermin and Wagner [11, 12] have established that the longwavelength fluctuations destroy the long-range order in 2G crystals. Moreover, the long-wavelength fluctuations of transversal displacements of atoms also diverge [128]. This implies a thermodynamic instability of such crystals. Graphene, being a single-atom-layer structure, presents the more close realization of a 2D material. Therefore, the abovementioned instability means the impossibility of the existence of this material in an isolated form. Indeed, one can prove that the root-mean-square deflection of the position of an atom in the direction perpendicular to the crystal plane, namely

$$\sqrt{\langle h^2 \rangle} \propto L \sqrt{\frac{T}{\kappa}},$$
(5)

increases linearly with the size L of the graphene sheet. Here, κ is the bending elasticity.

The above statements on the unlimited enhancement of fluctuations have been made in the framework of the harmonic approximation. However, the fluctuations can be constrained by taking into consideration the interrelation between bending and torsion. Therefore, graphene can exist within the framework of an anharmonic approximation providing it possesses large fluctuations in the perpendicular direction. Indeed, the above results of experimental studies on the graphene structure (see Section 2.3) point to the occurrence of wavy inhomogeneities on the graphene surface with a wavelength of 50–100 Å.

A more accurate characterization of the graphene structure at finite temperatures has been obtained by simulation of the equilibrium graphene structure using the Monte Carlo method [14]. The calculations have demonstrated spontaneous formation of wavy ripples with a wavelength of about 80 Å on the graphene surface, which is in close agreement with experimental data. In this case, the root-mean-square deflection of the atomic position in a perpendicular direction (roughness) varies with the size of the sheet as a power function [128, 129]:

$$\sqrt{\langle h^2 \rangle} \propto L^{\xi}, \quad \xi \approx 0.6 - 0.7.$$
 (6)

The deflection is still much less than the graphene size L, while the absolute magnitude of the roughness can exceed considerably the atomic size, reaching $\sim 1 \text{ nm} [13]$.

The spontaneous occurrence of roughness of the graphene surface at finite temperatures is accompanied by changes in the bond lengths and the size of the graphene cell. The equilibrium structure of graphene at a specific temperature can be found through the minimization of the free energy of the system. Within the frame of the harmonic approximation, the free energy of graphene can be represented as a sum of the internal energy, zero-vibration energy, and free-vibration energy:

$$F(a, T) = E(a) + \sum_{\mathbf{q}, j} \frac{\hbar \omega_{\mathbf{q}, j}(a)}{2} + k_{\mathrm{B}}T \sum_{\mathbf{q}, j} \ln \left[1 - \exp\left(-\frac{\hbar \omega_{\mathbf{q}, j}(a)}{k_{\mathrm{B}}T}\right) \right].$$
(7)

Here, *a* is the size of the graphene cell, and the summation is performed over all the vectors of the Brillouin zone and all the phonon modes. Minimization of the free energy in the lattice parameter provides the equilibrium graphene structure in a quasiharmonic approximation for a specific temperature. This energy relation for graphene is followed by the expression for its thermal expansion coefficient

$$\alpha \equiv \frac{1}{a} \frac{\partial a}{\partial T} = \sum_{q,j} \frac{c_{\rm v}(q,j)\,\gamma(q,j)}{a_0^2(\partial^2 E/\partial a^2)} \Big|_0,\tag{8}$$

where $c_v(q, j)$ is the contribution of each vibrational mode to the thermal capacity, $\gamma(q, j)$ are the Grüneisen coefficients for each mode, and the subscript 0 corresponds to the equilibrium lattice structure. Since the Grüneisen coefficient for the ZA mode has a large negative value, as shown above, at low temperatures when the optical modes possessing the positive Grüneisen coefficients are not populated, the contribution of the negative Grüneisen coefficient of graphene is negative at low temperatures. The calculations [32] performed within the framework of quasiharmonic approximation indicate that the thermal expansion coefficient of graphene has a minimum at room temperature and equals $-3.7 \times 10^{-6} \text{ K}^{-1}$, which is three times as great in absolute value as that for graphite $(-1.3 \times 10^{-6} \text{ K}^{-1})$ in the plane at the same temperature.

At high temperatures, however, when higher anharmonic corrections have to be taken into consideration, the quasiharmonic approximation no longer provides sufficient accuracy. The direct calculation of the equilibrium graphene structure as a function of temperature has been performed in Ref. [130] with the use of the Monte Carlo method and empirical potentials. The calculated temperature dependences of the lattice parameter and the distance between neighboring atoms are presented in Fig. 12. As is seen, the



Figure 12. The temperature dependences of the graphene lattice parameter a and the average distance $R_{\rm m}$ to the nearest neighbors, calculated in Ref. [130].

lattice parameter has a minimum value at a temperature of about 1000 K. It should be noted that the distance between nearest neighbors also decreases as the temperature rises, which is caused by the action of a compressing pressure in the graphene plane.

5. Thermal conductivity of graphene

5.1. Methods and results of measurements of graphene thermal conductivity

According to the available experimental data, graphene possesses the highest thermal conductivity among solid states at room temperature. Its thermal conductivity (4840–5300 W m⁻¹K⁻¹ [18, 131]) exceeds that for isotopically pure diamond (3320 W m⁻¹K⁻¹ [132]) and single-walled carbon nanotubes (3500 W m⁻¹K⁻¹ [133, 134]).

Raman spectroscopy is widely used for studying the dynamics of lattice vibrations. Interaction of the incident optical radiation with atomic vibrations in a crystalline lattice results in its inelastic scattering on the atoms of the crystal. Therefore, the spectrum of the scattered radiation contains, along with the incident radiation line, satellite lines, which are spaced apart symmetrically with respect to the incident line by the crystal vibrational frequencies. Both the position and the intensity of the scattered light lines depend on the temperature and the wavelength of the incident radiation. The most intense Raman peaks in graphene, as in graphite, are G and D peaks (1580 and 1350 cm⁻¹), the first of which corresponds to the symmetrical expansion–compressing vibrations of sp² bonds, while the second one relates to structural defects of graphene.

Raman spectroscopy was successfully applied previously for measuring the thermal conductivity of badly conducting materials and thin films [135, 136], as well as carbon nanotubes [137]. The applicability of this approach is firstly based on the high sensitivity of the position of the G peak in the Raman spectrum to the local temperature, and secondly on the possibility of heating locally some graphene sites several micrometers in size by a laser beam with a wavelength of less than 1 µm. These considerations form the basis for a very sophisticated method of measuring the thermal conductivity of graphene by means of confocal micro-Raman spectroscopy [18, 131]. According to this approach, a laser



Figure 13. Schematic of the experimental setup for measuring the thermal conductivity of graphene [131].

beam of a specified power is focused onto the middle of a single-layer graphene sheet suspended between two supports. The size of the irradiated spot is $0.5-1 \mu m$, and the temperature increase in the spot amounts to several dozen kelvins. The temperature of the heated site of graphene is determined on the basis of measurements of the shift in the position of the G peak. At moderate heating, the increase in temperature linearly depends on the laser power, and the coefficient in this dependence is proportional to the thermal conductivity of graphene.

Figure 13 illustrates schematically the experimental arrangement [131]. A set of longitudinal trenches 300 nm in depth and up to 5 μ m in width were fabricated by ion etching on the surface of an Si/SiO₂ substrate. Graphene sheets produced by the micromechanical exfoliation of highly oriented pyrolytic graphite (see Section 3.1) were applied onto the substrate in large numbers. Then, elongated graphene samples bridging the two sides of the trench and close in form to a rectangle were selected by means of a Raman microspectrometer. In so doing, the graphene sheets under investigation were in thermal contact with the graphite particles that also resided on the substrate surface. These particles absorb the heat released on irradiation of the graphene sheet by a focused beam of an Ar-ion laser $(\lambda = 0.48 \ \mu m)$. The size of the focal spot is about 0.5 μm ; however, the size of the hot region is increased to 1 µm due to electron diffusion. The measurements yielded magnitudes of the thermal conductivity coefficient ranging between 4840 and 5300 W m⁻¹ K⁻¹. The processing of the experimental data also allowed the estimation of the magnitude of the phonon mean free path with respect to the scattering: $l_{\rm p} \approx 775$ nm. Hence, $l_{\rm p}$ turned out to be much less than the characteristic size $(5-10 \ \mu m)$ of the graphene sample, which demonstrates the prevailing role of the diffusion mechanism of heat transport over the ballistic one.

The main source of the error in the above-described method of measuring the thermal conductivity of graphene relates to an uncertainty about the thickness of the graphene layer, which has to be known for evaluation of the thermal conduction coefficient on the basis of experimental evidence. The magnitude of the thickness (0.35 nm) used by the authors of Ref. [131] is a conditional one corresponding to the interlayer distance in crystalline graphite, which hardly correctly characterizes the thickness of an individual graphene layer.

The measurements indicate that the thermal conduction coefficient of an individual graphene layer exceeds by more than two times the appropriate value for crystalline graphite:

 $\kappa \approx 2000 \text{ W m}^{-1} \text{ K}^{-1}$. Therefore, the thermal conductivity of a 2D hexagonal structure (graphene) exceeds notably that of a 3D structure consisting of graphene layers. Transition from a 2D to a 3D structure occurs upon increasing the number of graphene layers, which should be accompanied by a lowering of the thermal conduction coefficient. Such a behavior can be attributed to an additional mechanism of phonon scattering related to the interaction between neighboring layers. This behavior has been studied experimentally by the authors of Ref. [138], who utilized for this aim the Raman spectroscopy method described above. In this case, Si/SiO₂ wafers with a set of parallel trenches 300 nm in depth and up to 5 µm in width were also used. The heat delivered to the graphene sheet was removed through thin metal pads deposited near the edges of the trenches. Few-layer graphene samples were produced by micromechanical exfoliation of pyrolytic graphite. The number of layers in the samples under investigation was determined on the basis of Raman spectrum processing [129]. The longitudinal size of the suspended part of the graphene sheet ranged between 5 and 16 µm. The thermal conductivity of the graphene samples was determined by fitting the measured temperature shift of the G Raman peak ($\approx 1579 \text{ cm}^{-1}$) under the action of laser irradiation to the solution of the relevant heat conduction equation for the sample by the finite element method.

Figure 14 presents the dependence of the thermal conduction coefficient of films consisting of several graphene layers on the number of such layers, which was measured by the authors of Ref. [138]. These data have been reduced to the common lateral size of 5 μ m in order to exclude the dependence of the thermal conduction coefficient on this parameter. The dashed lines mark the borders limiting the domain of variability of the thermal conductivity of crystal-line graphite (on evidence from various authors). The results of simulations performed by various methods, as well as the result of measuring (for comparison) the thermal conductivity ity for individual single-layer graphene, are also presented. As may be seen, the thermal conductivity of a few-layer graphene



Figure 14. Dependence of the longitudinal thermal conductivity of fewlayer graphene films on the number of layers [138]. The dashed lines indicate the limits of spreading the thermal conductivity of crystalline graphite. Calculated results taking into account all the possible phonon scattering mechanisms, excluding the scattering on defects — diamonds; calculations [149, 152, 155] for multilayer graphene structures on the basis of the Klemens model, taking into account the roughness — triangles; maximum magnitude [131] — squares; averaged value for a suspended graphene sheet 5 μ m in length — dots. All the measurements were performed at room temperature.

structure approaches that of crystalline graphite already when there are several layers.

An alternative approach to measuring the thermal conduction coefficient of graphene was applied in Ref. [20], where the graphene samples were synthesized by reduction from graphene oxide. The thermal conductivity was determined in this work by combining the results of measuring the temperature of the sample heated by electrical current with the solution of a 1D heat conduction equation. The temperature of the sample was measured by means of a Pt thermocouple. The graphene samples were synthesized by reduction of graphene oxide that was produced using the standard Hummer method described in detail in Section 3.3. The graphene reduction procedure was followed in flowing nitrogen at a temperature of 450 °C and lasted from 5 to 60 min.

The thermal conductivity of the samples was measured under vacuum conditions at a residual gas pressure of less than 0.03 Torr. The measurement device included an SiN substrate on which the longitudinal silicon pads used as contacts were placed. The distance between the pads ranged between 0.5 and 3 µm. A graphene sample was applied to the substrate in such a way that the electrical and thermal contacts with the pads were maintained. In one measurement configuration, a graphene sheet was suspended between those pads not having contact with the substrate, while in another one a graphene sheet partially lay on the substrate. The structure of the measuring system permitted taking measurements of both the thermal conductivity and the electrical conductivity of the sample simultaneously. The results of these measurements at room temperature are given in Table 3 for four samples. These samples differ in size, contact resistance, and the duration τ of thermal treatment at reduction of graphene. Furthermore, samples 2 and 3 were suspended, while samples 1 and 4 were in contact with the substrate surface.

The measurement results presented in Table 3 reveal a notable dependence of the transport coefficients of graphene on the duration of the thermal treatment of samples: the more prolonged the treatment duration, the higher the coefficients of thermal and electrical conductions of the sample. This is explained by the removal of oxygen atoms from the graphene surface, whose presence determines the mechanism of electron and phonon scattering and lowers the magnitude of the relevant transport coefficients. However, even thermal treatment for one hour does not allow the total removal of oxygen. Therefore, even in this case both the thermal conduction coefficient and the electrical conductivity of graphene remain several orders of magnitude lower than those for graphene samples produced by either the mechanical exfoliation of graphite or the CVD method. This permits the conclusion of a high sensitivity of the transport coefficients of graphene samples to both the method used for their production and synthesis conditions.

The thermal conductivity of an individual graphene sample is determined by the character of phonon propagation along the graphene plane. In this case, the phonon mean free path depends on such factors as the graphene size, the type and concentration of defects, and the occurrence of neighboring structures, as is the case in crystalline graphite or in a film consisting of a number of graphene layers. In the absence of those factors, the characteristic phonon mean free path for elastic scattering is determined by the phononphonon interaction processes (Umklapp processes) and their inclusion into consideration results in an increasing dependence of the thermal conduction coefficient on the graphene size. This brings up the question of the difference in the magnitudes of the thermal conduction coefficient for a graphene sheet suspended over a trench and for that lying on a dielectric substrate. It is reasonable to ascribe this difference to the influence of the substrate on the character of phonon propagation over a graphene sheet. The measured magnitudes of the thermal conduction coefficients for graphene samples suspended over a trench are compared in Ref. [139] with those for a graphene sample lying on a dielectric substrate (SiO_2) . This article also reports on the measured temperature dependence of the thermal conduction coefficient of graphene.

The graphene samples were grown by the CVD method [81] on the surface of a copper foil 25 µm thick. These samples were coated with a polymethylmetacrilate (PMMA) film with the goal of conservation, after which the copper substrate was removed by means of a 1M solution of Fe(NO₃)₃. The measuring device comprised an SiN_x membrane containing a 100×100 matrix of circular holes 3.8 µm in diameter spaced at 10 µm intervals. This membrane was situated on a round silicon frame 3 mm in diameter coated with a gold film 300 nm thick and 0.5×0.5 mm in area. Since the thermal conductivity of silicon nitride ($\sim 5~W~m^{-1}~K^{-1})$ is 2–3 orders of magnitude lower than that of graphene, a gold layer ~ 500 nm thick was deposited onto the SiN_x surface to provide thermal removal from the heated site of graphene. The graphene sample together with the PMMA film were applied onto a membrane, after which the film was removed by means of acetone, making the device ready for measuring the thermal conductivity of graphene. This device presented a graphene sheet covering a variety of holes in the membrane. The number of graphene layers and the defect content were monitored by means of a Raman spectrometer. For performing the measurements, the holes covered with graphene sites having a minimum number of defects were selected. The Raman spectra of such sites contain practically no D bands, indicating a single-layer defect-free graphene structure.

The thermal conductivity of graphene was measured by focusing a laser beam at $\lambda = 532$ nm by means of a lens $\times 50$ or $\times 100$ onto either the center of a hole above which the graphene sheet was suspended or the graphene site resting on the Au/SiN_x membrane. The absorption coefficient of laser

Table 3. Transport characteristics of graphene samples reduced from graphene oxide [20].

Sample	Thermal conductivity κ , W m ⁻¹ K ⁻¹	Electrical conductivity σ , 10 ² Ω^{-1} m ⁻¹	Thermal treatment duration τ , min	Contact resistance $R, \kappa \Omega$
1	2.87	62.2	60	120
2	0.87	6.21	5	2
3	0.14	6.57	5	130
4	_	19.5	20	300

radiation by graphene was measured with the aid of a semiconductor laser power meter situated under the membrane. The magnitude $(3.3 \pm 1.1\%)$ of this parameter was obtained by extracting the fraction of power absorbed by the empty membrane from that for the membrane containing the graphene sheet. The local temperature of the graphene sheet exposed to laser irradiation was measured using the temperature shift $(4.05 \pm 0.2) \times 10^{-2}$ cm⁻¹ K⁻¹ of the G-peak position in the graphene Raman spectrum, which was evaluated independently in a set of special measurements. The value of the thermal conductivity of graphene was obtained by fitting the measured temperature profile with the relevant solution of the heat conduction equation for the graphene sheet heated by the laser beam.

Figure 15 compares the measured magnitudes of the thermal conductivity of a graphene sheet suspended over a hole in the membrane [139] with the relevant data for pyrolytic graphite [140–142]. The measured magnitude of the thermal conductivity of graphene at room temperature accounts for $(2500 + 1100/ - 1050) \text{ W m}^{-1} \text{ K}^{-1}$, while at a temperature of 500 K it equals $(1400 + 500/ - 480) \text{ W m}^{-1} \text{ K}^{-1}$. Thus, the thermal conductivity of graphene exceeds that for graphite within the entire temperature range under investigation. The decreasing temperature dependence of the graphene thermal conduction coefficient observed is explained by shortening the phonon–phonon scattering mean free path, which in turn is caused by an increase in the phonon density and enhancement of the influence of lattice anharmonicity on the phonon–phonon interaction.

In parallel with the graphene samples suspended over membrane holes, the authors of Ref. [143] measured the thermal conductivity of single-layer graphene samples lying on an SiO₂ substrate. These samples were fabricated by the micromechanical exfoliation of graphite (see Section 3.1). A single-layer defectless structure of the samples under investigation was confirmed by Raman spectroscopy measurements. Graphene ribbons between 1.5 and 3.2 µm in width and between 9.5 and 12.5 µm in length rested on the surface of an SiO₂ longitudinal asperity ~ 300 nm thick, the two ends of which were connected to four Au/Cr resistance thermometer (RT) lines. Such a configuration permitted the measurement of the temperature at the graphene ribbon edges. The



Figure 15. Comparison of the measured temperature dependence of the thermal conductivity of graphene suspended over a hole in a membrane [139] with the relevant data for pyrolytic graphite: $[140](\bullet)$; $[141](\bullet)$; $[142](\bullet)$; $[142](\bullet)$. The data marked by ∇ and \odot were obtained by the use of focusing lenses with different magnifications.



Figure 16. Comparison of the measured temperature dependence of the thermal conductivity of a graphene sheet lying on an Si/SiO_2 substrate [143] with the relevant data for pyrolytic graphite (PG) [140] 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.

measured values of the electrical resistance of three graphene samples designated as G1, G2, and G3 in Fig. 16 turned out to equal 160, 7, and 5400 k Ω , respectively. Such a significant spread indicates the high sensitivity of measured results to the quality of contacts, which is the main source of measurement errors. The measurement result relating to the sample G2 (7 k Ω) is close to the ballistic limit $R_{\rm b} = h/4e^2 = 6.47$ k Ω and appears to be the most adequate. Combining this finding with the measured Seebeck coefficient for the sample G2 permitted the determination of the Fermi level position $E_{\rm F} = 0.049$ eV, the number density of carriers at the Fermi level, n = $(E_{\rm F}/\hbar v_{\rm F})^2/\pi = 1.7 \times 10^{11} {\rm cm}^{-2}$, their thermal velocity $v_{\rm F} =$ $1 \times 10^8 \text{ cm s}^{-1}$, and the mobility $\mu \sim 20,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The thermal conductivity of the G2 sample at room temperature established on the basis of processing these data turned out to be 579 ± 34 W m⁻¹ K⁻¹, which is several times lower than that for crystalline graphite. Such a low value of the thermal conduction coefficient of the graphene sample lying on an SiO₂ substrate is obviously caused by the influence of the substrate, providing an additional mechanism for phonon scattering. Figure 16 compares the measured temperature dependences of various graphene samples lying on an SiO₂ substrate with the relevant data for pyrolytic graphite (PG). As is seen, the temperature dependences of the thermal conductivity of graphene and pyrolytic graphite differ in the position of the maximum, which is shifted towards higher temperatures in the case of graphene. This implies a difference in the character of the influence of neighboring layers in graphite and in an SiO₂ substrate on phonon propagation in a graphene layer.

In the above-described experiments on the measurement of the graphene thermal conduction coefficient by means of Raman spectroscopy, the characteristic size of the region heated by the laser beam was about 1 μ m, which is only several times less than the lateral size of the suspended part of

Method of synthesis of graphene	Measuring method	Measuring conditions	Graphene size, μm	Temperature range, K	κ , W m ⁻¹ K ⁻¹	References
MEPG*	Raman spectra	Suspended sample	≤ 5	300	4840-5300	[18, 131]
MEPG	Raman spectra	Suspended graphene samples with 2 to 4 layers	5-15	300	2800-1300	[138]
CVD	Raman spectra	Suspended sample	3.8	300-500	$(2500-1400)\pm 50\%$	[64]
MEPG	Seebeck effect	Sample lying on a SiO ₂ substrate	1.5-3.2 (width); 9.5-12.5 (length)	80-300	(100-579)±15%	[143]
MEPG	Raman spectra	Suspended sample	44	300	630	[144]
CRGO**	Ohmic heating	Suspended sample	Up to 3	300	0.87	[20]
CRGO**	Ohmic heating	Sample lying on a SiN substrate	Up to 3	300	2.87	[20]
* Machanical aufali	ation of mynalytic a	nombito				

Table 4. Graphene thermal conductivity measured by various authors.

* Mechanical exfoliation of pyrolytic graphite.

** Chemical reduction of graphene oxide.

the graphene sheet. One would expect a considerable experimental error in measuring the thermal conduction coefficient at such a ratio of the sizes. However, the results of the above experiments are in agreement with those obtained for a graphene sample suspended over a trench 44 μ m in depth [144]. And although the measured thermal conductivity of graphene ($\kappa \approx 630 \text{ W m}^{-1} \text{ K}^{-1}$) turned out to be several times lower than the maximum measured values, this result also confirms the reputation of graphene as a material that conducts heat well.

Table 4 summarizes the results of measuring the thermal conductivity of graphene. Comparison of experimental data obtained by different authors points to a considerable spread in the magnitude of the thermal conductivity of graphene. This is due to a set of factors, including the dependence of the structure of graphene on the method and specific conditions of its fabrication, and also the considerable experimental error inherent to investigations of nanometer-sized objects. It is hoped that advances in the development and modification of approaches to the production of graphene will result in the synthesis of large-area graphene samples with a negligible defect content already in the immediate future. Further development of experimental techniques will also permit reliable measurements of the transport coefficients of such samples depending on the size, temperature, and number of graphene layers.

5.2 Methods of computing graphene thermal conductivity

As follows from estimates made on the basis of measured electrical conductivity data by the use of the Wiedemann– Franz law, the contribution of electrons to the thermal conduction of graphene, as well as CNTs, is negligible compared to that of phonons [19] (less than 1% at room temperature). Consequently, the thermal conduction of graphene is determined mainly by the phonon contribution. For this reason, the thermal conductivity of graphene can be evaluated by accounting for the phonon contribution to the heat transport. In doing so, one can rely on either the Boltzmann kinetic equation for the phonon distribution function or the numerical solution of dynamic equations for the coordinates of nuclei. Both approaches will be briefly analyzed below, and the results obtained will be highlighted. **5.2.1 Kinetic equation for phonon thermal conduction.** If the vibrational excitation of the system under consideration is low, phonons form a rarefied gas obeying the Boltzmann kinetic equation

$$\frac{\partial N}{\partial t} + \mathbf{u} \, \frac{\partial N}{\partial \mathbf{r}} = \operatorname{St} N, \tag{9}$$

where $N \equiv N_{\lambda}(t, \mathbf{r}, \mathbf{k})$ is the distribution function for phonons of the λ th mode, and St *N* is the collision integral for phonons. As distinct from a conventional gas, neither phonon number nor total quasimomentum is conserved, in principle, in phonon collisions. The latter fact relates to the occurrence of Umklapp (U) processes, for which the quasimomentum can change by the reciprocal lattice vector **b**:

$$\sum_{i} \mathbf{k}_{i} = \sum_{i} \mathbf{k}_{i}' + \mathbf{b} \,, \tag{10}$$

as opposed to normal processes (N-processes) for which the quasimomentum is conserved.

A standard approach to the solution of the phonon Boltzmann equation is based on the linearization of the collision integral in the vicinity of the equilibrium phonon distribution function. This approach is applicable in the case of a relatively low temperature gradient, when a local phonon distribution function is close to the equilibrium one and the temperature determining this distribution function is a parameter gradually varying along the sample. A linear set of equations obtained as a result of linearization of the Boltzmann kinetic equation generally describes the inter-relation between perturbations of the phonon distribution function. However, one can neglect this interrelation by considering various phonon modes as independent ones having specific relaxation times $\tau_{\lambda}(\mathbf{k})$. In this case, it can be shown that the thermal conduction coefficient is determined by the summation of contributions from all the phonon modes [145]:

$$\kappa = \frac{1}{8\pi^3} \sum_{\lambda} \int C(\omega_{\lambda}(\mathbf{k})) \tau_{\lambda}(\mathbf{k}) (\mathbf{v}_{\lambda} \mathbf{s})^2 \, \mathrm{d}\mathbf{k} \,, \tag{11}$$

where **s** is the direction of the heat flow, $\mathbf{v}_{\lambda} = d\omega_{\lambda}(\mathbf{k})/d\mathbf{k}$ is the group velocity of the mode λ , and $C(\omega, T)$ is the specific heat capacity of the relevant mode:

$$C(\omega, T) = \frac{(\hbar\omega)^2}{k_{\rm B}T^2} \frac{\exp\left(\hbar\omega/k_{\rm B}T\right)}{\left(\exp\left(\hbar\omega/k_{\rm B}T\right) - 1\right)^2} \,. \tag{12}$$

The following equation can be easily obtained for a 2D case and an isotropic medium as a result of substitution of the integration over the angular frequencies for that over the wave vectors:

$$\kappa = \frac{1}{4\pi h} \sum_{\lambda} \int C(\omega, T) \,\tau(\omega, T) \,\frac{v}{u} \,\omega \,\mathrm{d}\omega \,, \tag{13}$$

where *h* is the characteristic lateral size, and $u = \omega/k$ is the phase velocity of the phonon λ mode.

5.2.2 Phonon scattering processes. The phonon relaxation time entering into formula (11) is determined by all the phonon scattering processes. In a perfect infinite crystal, the phonon mean free path is limited by phonon–phonon collisions which present one of the manifestations of the lattice anharmonicity of interatomic vibrations. A real crystal contains point and extensive defects, such as vacancies, impurities, and boundaries. All these defects cause phonon scattering, so that each of the scattering processes is characterized by the relevant relaxation time τ_i . Taking into account all the scattering mechanisms, the average phonon relaxation time entering into the heat conduction equation is written out as

$$\frac{1}{\tau} = \sum_{i} \frac{1}{\tau_i} \,. \tag{14}$$

We shall consider below the most widely used analytical expressions for the phonon relaxation times derived on the basis of the perturbation theory within the framework of various approximations and simplifications. One should remember that these expressions are rather rough and present only estimates for computing the phonon relaxation times.

5.2.2.1 Phonon–phonon interaction. Phonon–phonon interaction can be evaluated by taking into account anharmonic terms in the expansion of the energy of interatomic interactions. Because the Debye temperature for graphene ($\sim 2000 \text{ K}$) is far above room temperature, the contribution of the anharmonicity is quite low and can be accounted for within the framework of the perturbation theory. Usually, only the cubic term corresponding to the three-phonon interaction is taken into consideration because the higher-order terms of expansion make a considerably lower contribution [146].

As mentioned above, the phonon-phonon interaction processes can be divided into two classes: normal processes, with the conservation of quasimomentum, and umklapp processes, for which the quasimomentum changes by the reciprocal lattice vector. Umklapp processes involve phonons having high quasimomentum (on the order of $1/a_0$, where a_0 is the magnitude of the lattice vector), while for normal processes it is not necessary to include shortwavelength phonons. This requirement means that an umklapp process with the three phonon interaction should involve two short-wavelength phonons. For this reason, the umklapp processes can be essential only at high temperatures when short-wavelength modes are excited, while the significance of the normal processes does not depend on the population of short-wavelength modes. However, the normal processes do not make a considerable contribution to the thermal conduction of common materials due to some reasons. One of the reasons was argued by R Peierls in due

course [147]: N-processes conserve the thermal flow in a system without dispersion; therefore, they do not provide a finite thermal conduction. A stronger statement was formulated by Pomeranchuk [148], who had proved that the N-processes with a linear dispersion involving only long-wavelength phonons cannot provide a finite phonon scattering time for common materials as $k \rightarrow 0$. It should be noted, however, that this statement is no longer valid for 2D systems like graphene due to the occurrence of a quasiquadratic ZA mode in the spectra of such systems. Therefore, the role of N-processes in the thermal conduction of graphene remains unclear; nevertheless, practically none of the analytical models of the thermal conduction of graphene involve the N-processes in phonon interactions.

Klemens and Pedraza [149] have derived the following relation for the long-wavelength phonon scattering time in the umklapp process:

$$\frac{1}{\tau} \approx 2\gamma^2 \, \frac{k_{\rm B}T}{Mv^2} \frac{\omega^2}{\omega_{\rm D}} \,, \tag{15}$$

where γ is the Grüneisen parameter, *M* is the mass of a cell, $k_{\rm B}$ is the Boltzmann constant, *v* is the group velocity, and $\omega_{\rm D}$ is the Debye frequency.

5.2.2.2 Phonon scattering on a boundary. At quite low temperatures, the phonon mean free path in pure samples is mainly limited by the scattering on a 'wall', i.e., on a boundary of the sample. This phenomenon results in a dimension effect that manifests itself in a dependence of the thermal conductivity on the size of the sample and was first examined experimentally by de Haas and Biermasz [150].

The boundary phonon scattering is determined by the characteristic relaxation time as follows [151]:

$$\frac{1}{\tau} \approx \frac{1-p}{1+p} \frac{v}{L} \,, \tag{16}$$

where p is the degree of roughness of the boundary (the fraction of phonons reflected specularly), and L is the smallest size of the sheet.

Naturally, the phonon mean free path relating to the boundary reflection for absolutely rough surfaces (p = 0) is equal to the size of the sheet.

5.2.2.3 Phonon scattering on defects. The phonon mean free path is also limited by the scattering of phonons on defects, which was described in detail in Section 2.2, along with phonon–phonon scattering processes and the phonon scattering on a boundary. The characteristic relaxation time for this process can also be calculated by the perturbation theory. Thus, the change in the mass is taken into consideration in the case of the elastic phonon scattering on isotopes (Rayleigh scattering), which results in the following relation for the relevant relaxation time:

$$\tau \approx \frac{2v^2}{\omega^3 \Gamma S} \,, \tag{17}$$

where

$$\Gamma = \sum_{i} c_i (1 - c_i) \left(\frac{\Delta M_i}{M}\right)^2,\tag{18}$$

v is the group velocity, S is the cross section of the isotope, c_i is the concentration of cells with the *i*th defect, M is the mass of

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the cell, and ΔM_i is the change in the mass of the cell with the *i*th defect.

The phonon scattering on point defects was analyzed in detail by Klemens [152]. He considered three mechanisms determining the contribution of a defect to the scattering: (a) perturbation of the kinetic energy due to a change in the mass; (b) perturbation of the potential energy due to a change in the elastic constants for some bonds, and (c) perturbation of the potential energy due to an elastic strain field.

However, considering only the mechanism of the influence of defects due to a change in the atomic mass on account of isotopic substitution, one concludes that the contribution of phonon-phonon scattering processes becomes negligible, even at very low defect concentrations. In this case, the phonon scattering on defects prevails, so that the thermal conduction coefficient decreases as the defect number density increases.

Generally, the size of a defect should be compared to the phonon wavelength, so that the above expression for the scattering probability is valid for the point defects and the defects whose size is less than the phonon wavelength ($\lambda > 2r$) [153]. For phonons with the wavelength less than the size of the defect ($\lambda < 2r$), the scattering obeys the geometrical optics laws, according to which the phonon relaxation time is expressed as follows [154]:

$$\tau = \frac{S}{v2rc_i} \,. \tag{19}$$

5.2.3 The divergence problem of the thermal conduction in a 2D system. As follows from Eqns (13)–(15), for three-phonon scattering alone in umklapp processes one obtains

$$C(\omega) \to \text{const}, \ \tau(\omega) \to \frac{1}{\omega^2}, \ \kappa \to \int \frac{\mathrm{d}\omega}{\omega} \ \text{as} \ \omega \to 0.$$
(20)

This leads to a well-known problem of a logarithmic divergence of the thermal conduction in a 2D system. Generally, this divergence can be removed by taking into account other mechanisms of low-frequency phonon scattering. These additional phonon scattering mechanisms can be taken into consideration by inserting a long-wavelength (lowfrequency) cutoff frequency ω_c for acoustical phonons. The choice of ω_c for graphite has been physically justified by Klemens and Pedraza [149]. According to their assumption, low-frequency phonons interact in a direction transverse to the graphite plane, which promotes heat propagation in all directions. This diminishes the contribution of low-energy modes to the heat transfer along the plane to a negligible level. The phonon optical ZO' branch (4 THz) in the graphite spectrum was just taken as a cutoff frequency. The thermal conductivity calculated by Klemens and Pedraza for the basal plane of graphite amounts to about 1900 W m⁻¹ K⁻¹, which is close to the experimental value. In the subsequent publication [155], Klemens proposed choosing the value of $\omega_{\rm c}$ for graphene, assuming that the phonon mean free path cannot exceed the characteristic size L of the graphene sheet. In the case of three-phonon scattering, this leads to the following limitation that determines the lower limit of integration, ω_c , in formula (13):

$$l(\omega, T) = \frac{1}{2\gamma^2} v \frac{Mv^2}{k_{\rm B}T} \frac{\omega_{\rm D}}{\omega^2} < L.$$
(21)

Another approach to avoiding the logarithmic divergence is based on taking into consideration the higher-order terms of the perturbation theory. An increase in the thermal conductivity should saturate when the size of the sheet at which the contribution of the higher-order processes to phonon scattering becomes comparable to that in the first order. Specifically, taking into account the secondorder three-phonon scattering processes removes the divergence due to the addition of a constant (frequencyindependent) term determining the low-frequency phonon scattering [156]:

$$\tau_2^{-1} \approx \gamma^4 \left(\frac{k_{\rm B}T}{Mv^2}\right)^2 \omega_{\rm D} \,. \tag{22}$$

Including this term results in the prevalence of the secondorder processes for frequencies lower than

$$\omega_{\rm min} = \frac{2}{3} \gamma \sqrt{\frac{k_{\rm B}T}{Mv^2}} \omega_{\rm D} \approx 3 \times 10^{12} \, {\rm s}^{-1} \,. \tag{23}$$

Integration of expression (13) taking account of formula (23) permits the quantitative estimation of the thermal conduction coefficient of a graphene sheet, reaching the maximum within the range of 5000–10,000 W m⁻¹ K⁻¹ at a sheet size of about 1 mm.

5.2.4 Calculation of the thermal conductivity of graphene by the molecular dynamics method. Phonon thermal conduction in carbon nanostructures can be calculated by use of the nonequilibrium molecular dynamics (NEMD) method [157], equilibrium molecular dynamics (EMD) method [145], and homogeneous nonequilibrium molecular dynamics method (synthetic NEMD method) [159, 160]. Notice that the molecular dynamics method has acquitted itself quite well in calculations of the thermal conductivity of carbon nanotubes whose structure is similar to that of graphene [158]. The accuracy of all the molecular dynamics calculations directly depends on the type and parameterization of the model interaction potential utilized.

When the thermal conductivity of graphene is calculated by the NEMD method, a sample is conceptually placed between cool and hot thermostats, which provides a temperature gradient inside the sample. The movement of atoms in the sample between the thermostats obeys Newtonian dynamics laws, which allow the calculation of the thermal flux in the direction of the temperature gradient. After establishing the stationary regime, the thermal conductivity κ of the sample is evaluated by applying the Fourier law for the thermal flux:

$$J = -\kappa \nabla T, \tag{24}$$

where J is the thermal flux and ∇T is the temperature gradient (the derivative with respect to x in a 1D case).

The NEMD method has two main versions: the direct NEMD method, and the reverse NEMD method [161]. In the first case, the temperatures of the cool and hot thermostats are set, and the thermal flux through the sample is calculated. In the second case, the thermal flux is kept constant, and the temperature gradient is evaluated. Moreover, the NEMD method can be realized either with or without the use of periodic boundary conditions, and also by utilization of thermostats of various types. However, this simplest approach, modeling the experiment directly, has some disadvantages. If the length of the sample under modeling is less than the phonon mean free path, the thermal conductivity is underestimated. In addition, if the length of the sample under modeling is not sufficient to take into account long-wavelength phonons, the thermal conductivity calculated is underestimated as well.

The calculation of the thermal conductivity by the EMD method is based on the fluctuation–dissipation theorem for a spontaneous thermal flow in a substance. In this case, the thermal conduction coefficient is expressed through a spatialtime integral of the autocorrelation function defining a thermal flux, in accordance with the Green–Kubo formula:

$$\kappa(T) = \frac{1}{3Vk_{\rm B}T^2} \int_0^\infty \left\langle \mathbf{J}(t) \, \mathbf{J}(0) \right\rangle \mathrm{d}t, \qquad (25)$$

where V is the volume, T is the temperature, $k_{\rm B}$ is the Boltzmann constant, and $\mathbf{J}(t)$ is the thermal flux vector defined as

$$\mathbf{J}(t) = \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i} \mathbf{r}_{i} E_{i} = \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i} \mathbf{r}_{i} (E_{\mathrm{k},i} + E_{\mathrm{p},i}), \qquad (26)$$

where $E_{k,i}$ is the kinetic energy, and $E_{p,i}$ is the potential energy of the *i*th particle.

The main drawback of the equilibrium molecular dynamics method consists in the slow convergence of the autocorrelation function. Furthermore, the results of calculations depend on the initial conditions, which necessitates the performance of a large amount of calculations with statistically independent initial conditions.

To overcome the drawbacks inherent to the NEMD and EMD methods, the homogeneous nonequibrium molecular dynamics method combining the NEMD method with the Green–Kubo formula for the thermal conduction has been proposed. In doing so, an additional small 'fictitious thermal force' acting on all the atoms is introduced. The thermal conductivity along the z-axis is calculated as a limit of the fictitious force approaching zero [160, 162]:

$$\lambda = \lim_{\mathbf{F}_{e} \to 0} \lim_{t \to \infty} \frac{\langle J_{z}(\mathbf{F}_{e}, t) \rangle}{F_{e} T V}, \qquad (27)$$

where T is the temperature of the sample, V is the volume, $J_z(\mathbf{F}_e, t)$ is the z-component of the thermal flux vector for a point in time t, and \mathbf{F}_e is the 'fictitious thermal force'.

However, the evaluation of the limit as $F_e \rightarrow 0$ is not very easy. The direct calculation of the thermal conductivity in the case of a low fictitious force results in a considerable error. For this reason, the method of analytical extrapolation of the dependence of the thermal conductivity on the fictitious force for $F_e \rightarrow 0$ has usually been used.

5.3 Calculated results on graphene thermal conductivity

5.3.1 Thermal conductivity of an ideal graphene sheet and its size dependence. The results of calculations of the thermal conductivity of graphene obtained by using the above-described methods will be considered below.

First of all, the analytical work of Klemens [155] should be mentioned, where a simple analytical model of the thermal conductivity of graphite was proposed. This approach is also applied to calculations of the thermal conductivity of an ideal graphene sample. Since the main contribution to the thermal conduction is due to two acoustic branches in the graphene plane (longitudinal LA and transverse TA modes), and the Brillouin zone possesses a hexagonal structure (Fig. 9), the Brillouin zone is substituted according to the Debye model by a circle of an equivalent area with the reciprocal radius

$$q_{\rm D} = \frac{2}{a} \left(\frac{2\pi}{\sqrt{3}}\right)^{1/2} = 1.55 \times 10^8 \ {\rm cm}^{-1} \,,$$
 (28)

where *a* is the lattice parameter $(2.46 \times 10^{-8} \text{ cm})$, and the Debye velocity *v* is defined as the average speed of sound for two acoustic modes:

$$\frac{2}{\langle v \rangle^2} = \frac{1}{\langle v_{\rm LA} \rangle^2} + \frac{1}{\langle v_{\rm TA} \rangle^2} \,. \tag{29}$$

Because the thermal conduction of graphene is mainly determined by the contribution from long-wavelength phonons having a linear dispersion, Klemens used the Debye velocity instead of the group one, and set the Grüneisen parameter to 2 (experimental value for graphite). Moreover, utilizing the high-temperature classical expression ($C \propto \omega$) for the thermal capacity, he arrived at the value of the thermal conductivity of graphite (1900 W m⁻¹K⁻¹) close to the experimental one. Application of the above approach to the calculation of the graphene thermal conductivity results in the following relation containing the dependence on the graphene sheet size:

$$\kappa = \frac{1}{\gamma^2} \rho \, \frac{v^4}{\omega_{\rm D}} \ln \left(\frac{\omega_{\rm D}}{\omega_{\rm c}} \right). \tag{30}$$

The cutoff frequency ω_c was determined from the condition that the phonon relaxation length at umklapp processes cannot exceed the characteristic size of the graphene sheet. The magnitudes of the thermal conductivity calculated for ideal graphene sheets 1 and 10 µm in size accounted for 4400 and 2590 W m⁻¹ K⁻¹, respectively.

Although the acoustical branches possess linear dispersion up to almost the boundary of the Brillouin zone, and the remaining branches are characterized by a zero group velocity in a long-wavelength region, which is why they do not contribute to the energy transfer, several attempts have been undertaken to refine Klemens's results by integrating the Boltzmann equation with the use of the real dispersion relation for $\omega(k)$ [19, 117, 163, 164]. This allowed the correct calculation of the frequency dependences of (group and phase) velocities and the Grüneisen parameter, which are generally not constants.

Specifically, the Grüneisen parameters were assumed to be frequency-dependent in Ref. [117], although the average speed of sound of two acoustical modes was utilized as the group velocity. To avoid the divergence of the thermal conductivity integral at small wave vectors, the calculated frequency of ZO' for two-layer ideal graphene $(\omega_c = 1.5 \times 10^{13} \text{ s}^{-1})$ was taken as the lower limit of integration. Such an approach is similar to that used by Klemens and Pedraza in the case of graphite [149], where the frequency of the ZO' mode at the G point was adopted as the cutoff frequency ω_c . Since the cutoff frequency was set to be constant, the thermal conductivity of graphene (2200 W $m^{-1} K^{-1}$ at 300 K) also turned out to be independent of both the size of the graphene sheet and the number of graphene layers. In should be noted that the abovedescribed approach is only justified for multilayer graphene samples and cannot be applied to single-layer systems.

The authors of Ref. [163] also applied the Klemens method [155] with constant values of the group velocity and



Figure 17. Dependences of the thermal conductivity κ of a defectless graphene sheet on size L (a) [163] and temperature (b) [19]

the Grüneisen parameter; however, these values for both of the acoustical modes, as well as the cutoff frequency, were calculated by averaging the results obtained from first principles. Figure 17a depicts the dependence of the thermal conductivity of ideal graphene on the graphene sheet size for various values of the Grüneisen parameter for two acoustical modes. As is seen, the thermal conductivity is a monotonically increasing function of the graphene sheet size independently of the choice of the Grüneisen parameter. The roomtemperature magnitude of the thermal conductivity for $L = 10 \,\mu\text{m}$ turned out to be close to 4000 W m⁻¹ K⁻¹, which notably exceeds the value calculated by Klemens for a graphene sheet of the same size.

The thermal conductivity of ideal graphene has been calculated in Ref. [19], taking into account the umklapp processes allowed by the energy and momentum conservation laws. The umklapp processes were accounted for by means of so-called scattering diagrams, which clearly demonstrate the allowed phonon states in the Brillouin zone for each scattering event. The phonon scattering on the sheet boundary is considered as a separate process, for which the relaxation time is calculated by formula (16) [151]. In this case, the total relaxation time is finite, since the relaxation time of phonons at the boundary is frequency-independent, so that it is not necessary to introduce the cutoff frequency, as Klemens did. In essence, however, these are just various methods to take into consideration the same assumption: namely, limitation of the phonon mean free path by the boundary. Figure 17b presents the temperature dependences of the thermal conductivity of ideal graphene for various sheet sizes.

The above data give evidence of a spread within a factor of 1.5 in the absolute values of the thermal conductivity reported in different theoretical papers. Moreover, such a spread is inherent to even various types of work performed by the same research team. The main source of such a spread relates to the distinction in the model interaction potentials in graphene used by various authors. The true potential has a many-body nature and depends not only on the distance between the pair of atoms under consideration but also on the position of other atoms in the lattice. At the present time, this dependence can be taken into consideration only within the framework of rough empirical models. An even more considerable spread is inherent to the measured data on the thermal conductivity of graphene, which were obtained by various authors (see Table 4). In any case, however, the thermal conductivity of ideal graphene rises as the graphene sheet size increases,

which may be explained by an increase in the number of phonons participating in the heat transfer as the graphene size grows.

Molecular dynamics calculations also reveal a monotonic increase in the thermal conductivity of graphenes and of carbon nanotubes as the size of the sample increases (Fig. 18). Calculations performed for samples of up to 2 μ m in length have shown that the thermal conductivity does not converge to some specific magnitude, which implies a notable contribution of the ballistic mechanism of heat transfer for the samples with such a length. A similar conclusion has been made on the basis of NEMD calculations for single-walled carbon nanotubes [165], whose thermal conductivity does not saturate even for the length of 1.6 μ m. Slow convergence of κ as the sample size rises in NEMD calculations was also noted in Refs [162, 166, 167].

The magnitudes of the thermal conductivity calculated by various authors with the use of the MD method are not in a complete agreement with one another. Thus, the thermal conductivity of the graphene sample 2 μ m in length calculated in Ref. [164] varies in the vicinity of 700 W m⁻¹ K⁻¹, which corresponds roughly to that for carbon nanotubes (Fig. 18). However, this evidence is somewhat lower than experimental values and calculated data based on the solution of the Boltzmann equation, which can be attributed to a peculiarity of MD calculation methods. Properties of the



Figure 18. Comparison of the dependences of the thermal conductivity of graphene and a CNT on length: calculations for graphene [162]—squares; approximation of those data by the function $y = 134.72x^{0.22}$ —dashed line; calculations for (5, 5) CNT [164]—dots, and Ref. [166]—solid line.

empirical interaction potentials important for calculating the thermal conductivity of carbon structures by MD methods were examined in Ref. [164]. The analysis has demonstrated that the utilization of Tersoff [168] and Brenner [169] interaction potentials results in underestimation of the speed of sound for phonon TA and LA modes and, in most cases, in overestimation of the Grüneisen parameter compared to experimental data and magnitudes calculated from first principles using the density functional theory. Thus, the utilization of the calculated thermal conduction coefficient.

The thermal conductivity of a graphene sample ranging in length from 11 to 60 nm has been calculated in Ref. [170] by means of the direct NEMD method. Evaluating the thermal conductivity by the Fourier formula, the thickness of the graphene sheet was set to only 0.144 nm, which is rather low in comparison to the standard value of 0.34 nm (twice the van der Waals radius of a carbon atom) usually adopted for this aim. In doing so, the thermal conductivity of a graphene sample 2 μ m in length evaluated by the extrapolation of the data for samples from 11 to 60 nm in length accounts for 1000–1270 W m⁻¹ K⁻¹, depending on the edge structure of graphene (armchair/zig-zag).

Some calculations predict much higher values of the thermal conductivity of graphene. Thus, Ref. [171] reports on the room-temperature value of 1700 W m^{-1} K⁻¹ for a graphene sheet 20 nm in length calculated with the aid of the NEMD method and the Brenner potential [169]. The value of the thermal conductivity of graphene ribbons 30 nm in length reaches about 5000 W m⁻¹ \overline{K}^{-1} [172]. However, the reliability of these data is doubtful for several reasons. First, the data obtained in Ref. [171] for the thermal conductivity of singlewalled carbon nanotubes (1600 W m⁻¹ K⁻¹ at 300 K) are not in agreement with those calculated by the NEMD method in later publications. The thermal conduction coefficient of nanotubes of a comparable length calculated in other studies by means of a similar method is at least an order of magnitude lower [165, 167, 173, 174]. Second, high magnitudes of the thermal conduction coefficient for short graphene samples are at variance with the results of Ref. [163] obtained by the construction of the analytical model. According to those, a graphene sample 1 µm in length possesses a room-temperature thermal conduction coefficient of about $1000 \text{ W m}^{-1} \text{ K}^{-1}$. The shorter samples exhibit a much lower value, which probably relates to a monotonic decrease in the thermal conductivity as the graphene sample length shortens due to diminishing the number of phonon frequencies contributing to the thermal conduction.

Very large values of the room-temperature thermal conductivity for quite short samples (2.4 nm in length at periodical boundary conditions in the direction of the heat flow) were also calculated in Ref. [162] by means of the homogeneous NEMD method: 6600 W m⁻¹ K⁻¹ for CNT (10,10), and 7500 W m⁻¹ K⁻¹ for graphene. The calculation method utilized involves an arbitrary choice of the function approximating the dependence of the thermal conductivity on the fictitious thermal force. This function increases abruptly as the fictitious force approaches zero, and the choice of this function appreciably determines the resulting value of the thermal conduction coefficient. The authors of Ref. [175] tried to recalculate the limit $F_e \rightarrow 0$ based on the data reported in Ref. [162]. This resulted in the thermal conductivity of 560 W m⁻¹ K⁻¹ for a nanotube at a temperature of 100 K, which is much lower than the value of 37,000 W m⁻¹ K⁻¹ at

100 K reported in Ref. [162]. Therefore, the values of the thermal conductivity of a CNT and graphene calculated in Ref. [162] should be considered with a great caution.

5.3.2 Influence of the width of a graphene sheet on the thermal conductivity. Graphene samples between several nanometers and several dozen nanometers in width may usually unite into a special class named 'graphene nanoribbons' (GNRs). In addition to special electronic properties [176], these nanoribbons also possess interesting phonon characteristics.

The thermal conductivity of graphene samples several nanometers in width has been calculated by means of MD methods. Usually, in such calculations either the graphene model is used with the periodical boundary conditions in the direction perpendicular to the heat flow, which corresponds to a graphene sheet of infinite width, or the model presenting a stripe several nanometers in width without the boundary conditions in the perpendicular direction, which corresponds to a GNR, is employed.

NEMD calculations have indicated that the thermal conductivity of a graphene sheet depends on its width; thus, the thermal conductivity decreases at a transition from an infinite-width graphene model to a GNR 2 nm in width. This decrease is more pronounced for graphene with the armchair structure [170]. It may be explained by the influence of additional phonon modes localized at the boundary of the GNR [177]. At the same time, Ref. [178] reports that doubling the GNR width from 1.5 nm to 3 nm does not notably change the thermal conductivity. Lower values of the thermal conductivity of the GNR in comparison with that of wider graphene samples can also be caused by phonon scattering on defects usually occurring at the boundaries of the GNR.

5.3.3 Temperature dependence of the thermal conductivity of graphene. Temperature dependences of the thermal conductivity of graphene samples of various lengths were calculated on the basis of the Boltzmann kinetic equation [19, 163]. Two main factors determine these dependences. The first relates to a rise in the number of phonons contributing to the heat transfer as the temperature increases. The second one has a bearing on the enhancement of the phonon scattering probability as the temperature grows. However, this latter factor manifests itself in the case of a graphene sample size exceeding the characteristic phonon mean free path for three-phonon scattering (the experimental data [18] imply that this value reaches about 800 nm at room temperature). Otherwise, the so-called ballistic regime occurs, when phonons can propagate unobstructed over the graphene sheet. In this case, the thermal conductivity is only determined by the first factor — the number of phonons contributing to the heat transfer. Within the framework of the above kinetic model, the thermal conduction is determined by the LA and TA modes, which should result in a rise in the thermal conductivity as the square of the temperature ($\sim T^2$) in a low-temperature region. However, the occurrence of the phonon ZA mode having a quadratic dispersion results in a weaker temperature dependence $T^{1.5}$ for the contribution of this mode to the ballistic thermal conduction, which causes the prevailing contribution of this mode to the heat transport at low temperatures [179, 180]. At a higher temperature (T > 20 K [180]), the thermal conductivity increases proportionally to T^2 due to contributions from the LA and TA modes.

Therefore, it should be concluded that the character of the temperature dependence of the thermal conductivity of



Figure 19. (a) Temperature dependences of the thermal conductivity κ of a graphene sheet 5 μ m in length calculated for various values of the parameter Γ describing phonon scattering on defects, and the parameter p describing the roughness of the boundary [19]; (b) temperature dependences of the thermal conductivity κ of graphene sheets of various lengths [163].

graphene is determined essentially by the size of the sample: for small-sized graphene samples, an increasing temperature dependence occurs, while beginning from some size this parameter exhibits nonmonotonic temperature dependence, with the maximum shifting towards the low-temperature region as the graphene size grows. Figure 19a presents such kinds of dependences calculated for long graphene samples. The role of three-phonon scattering diminishes as the graphene sheet length shortens. As a consequence, the shape of the temperature dependence changes as the sheet length shortens, and for graphene sheets less than 5 μ m in length the temperature dependence of the thermal conductivity increases monotonically (Fig. 19b). These results are in agreement with the monotonically increasing temperature dependence of the thermal conductivity within the temperature range of 180-400 K that was obtained by the use of the NEMD method with nonperiodical boundary conditions along the thermal flow for a graphene ribbon 5.7 nm in length [178].

5.3.4 Graphene thermal conductivity taking account of defects. As indicated above (see Section 2.2), the structure of real graphene sheets can contain both intrinsic defects and, depending on the method of preparation, various surface functional groups. These defects contribute to the probability of acoustic phonon scattering, whereas the thermal conduc-

tion coefficient of real graphene samples depends on the number density of the most probable defects. This dependence was evaluated both by utilizing MD simulations and through Boltzmann kinetic equation calculations. Thus, the results of NEMD calculations [164, 178] indicate an abrupt decrease in the thermal conductivity as the defect number density increases. In this regard, single and multiple carbon vacancies, OH-group adducts, and the roughness of the graphene sheet were considered as defects. Along with the NEMD method, the dependence of the thermal conductivity of graphene on the number density of OH groups and carbon vacancies was calculated by means of the Boltzmann kinetic equation utilizing formulas (15), (16) for the scattering probability due to a change in the atomic mass. The results obtained by the two methods are in qualitative agreement with each other and demonstrate that the defect number density promoting a decrease in the thermal conductivity by a factor of 2 is about 1% at room temperature for OH groups (Fig. 20b), and about 0.1% for the case of vacancies (Fig. 20a).

Notice that the dependences of the thermal conduction coefficient on the defect number density calculated in the above-cited works are in qualitative agreement with the results of simulations for single-walled carbon nanotubes, which also point to a decrease in the thermal conductivity as the defect number density increases [173].



Figure 20. The thermal conductivity of a defective graphene sheet $L = 1 \ \mu m$ in length as a function of the concentrations of vacancies (a), and OH groups (b) calculated by the use of the NEMD method and the Boltzmann kinetic equation method with two types of phonon distribution statistics (classic and quantum) [164].

Reduction of the thermal conduction coefficient of graphene as the defect number density increases has also been confirmed by measurements. While the measured value of this parameter for pure graphene sheets amounts to about $5000 \text{ W} \text{ m}^{-1} \text{ K}^{-1}$ [18], this quantity for graphene oxide ranges between 0.14 and 2.87 W m⁻¹ K⁻¹, depending on the degree of reduction of oxide [20].

5.3.5 Rectification of the thermal flow by means of graphene.

The results of NEMD simulations predict the ability of asymmetric graphene sheets to rectify the heat flow which follows from the anisotropy of the thermal conductivity in such objects. A model of a graphene sheet with a triangular shape [178] and a structure comprising two connected rectangular graphene sheets of different widths [181] have been studied. The length of the samples was varied between 3.4 and 13.5 nm. It was established that for all samples the heat flow is directed predominantly towards the side where the sample width decreases. In this case, the more effective rectification is demonstrated by triangular graphene models.

The heat flow rectification factor for triangular graphene sheets ranges from 100% (for long samples) up to 350% (for short samples) [181]. These magnitudes exceed those obtained by the NEMD method for carbon nanocones [182], conjugated nanotubes of various diameters [183], and nanotubes with a mass gradient [184]. Therefore, asymmetric graphene sheets can be believed at present to be the most promising possible structures for rectification of the heat flow.

6. Conclusion

A real boom is occurring in graphene investigations at the present time. Hundreds of articles are published monthly in this field, and tens of scientific conferences are held annually. This interest in the investigation of graphene seems to be warranted since graphene is a unique object combining the properties of a microscopic particle having quantum characteristics with those of a macroscopic material. The microscopic properties of graphene manifest themselves in the dependences of their main parameters on the sample size (dimensional dependences). Investigations into graphene permit one to answer the basic questions related to the peculiarities of 2D crystalline structures. In particular, the mere fact of the existence of graphene apparently contradicts the statement about the thermodynamic instability of such structures, formulated more than 70 years ago.

One more issue that can be resolved as a result of graphene investigations relates to the thermal conductivity of 2D structures. According to existing notions, the thermal conductivity of a 2D crystal governed by the phonon mechanism is characterized by increasing dependence on the sample size. This is caused by the dependence of the number of phonon modes existing in the sample on its size. Such a dependence is not inherent to macroscopic objects that are characterized by a relevant reference thermal conduction coefficient independent of its size. There are several physical mechanisms limiting the enhancement of the thermal conduction coefficient as the sample size enlarges. Due to the understandable difficulties of the experimental study of such miniature objects, the main source of information in this field is numerical simulations. However, the results of these simulations are rather sensitive to the type of interatomic interaction potential adopted. Furthermore, computer time expenses increase abruptly as the sample size enlarges, so that even

application of modern-day supercomputers does not permit advancing beyond a size exceeding several hundred nanometers. Therefore, the solution to this problem depends on the development of both computers and experimental techniques.

Along with basic problems, the interest in investigating graphene is also stimulated by the development of applied fields joined by the term 'nanotechnologies'. The high thermal, mechanical, and chemical stability of graphene, combined with miniature sample sizes and record transport characteristics, offer great prospects for practically employing this material. Active studies addressed to graphene applications are being performed at the present time in many laboratories throughout the world. These applications are based on the high sensitivity of the electronic characteristics of graphene to the sort and the number of molecules adsorbed, the nonlinear optical characteristics, high electrical and thermal conductivities, unique mechanical strength, electromechanical properties, etc. There can be little doubt that these studies will result in the development of new materials and new types of electronic devices.

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