

Mechanical and thermal stability of graphene and graphene-based materials

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Abstract. Graphene has rapidly become one of the most popular materials for technological applications and a test material for new condensed matter ideas. This paper reviews the mechanical properties of graphene and effects related to them that have recently been discovered experimentally or predicted theoretically or by simulation. The topics discussed are of key importance for graphene's use in integrated electronics, thermal materials, and electromechanical devices and include the following: graphene transformation into other sp^2 hybridization forms; stability to stretching and compression; ion-beam-induced structural modifications; how defects and graphene edges affect the electronic properties and thermal stability of graphene and related composites.

1. Introduction

Owing to the ability to form sp^1 , sp^2 , and sp^3 bonds, carbon is an ‘all-round’ chemical element. Under ambient pressure, carbon usually takes on the form of graphite (the most stable structure) or diamond, but other sufficiently stable allotropes can exist as well. In recent years, its numerous structures have been discovered.

The energy of binding between carbon atoms is very large; for example, in diamond, the cohesion energy is 717 kJ mol^{-1} . The phase transition between various stable phases of carbon requires the overcoming of an extremely high energy barrier. In other words, very high temperatures or pressures are required to initiate a spontaneous phase transition from one solid phase of carbon to another.

Apart from the best known crystal forms of carbon, i.e., graphite and diamond, amorphous forms exist, such as glassy carbon and black carbon. One-dimensional carbon is carbyne with the sp hybridization. It has proved to be possible to obtain amorphous carbon in the form of a film with a mixed type of hybridization [1]. A tetrahedral film of carbon can be formed upon bombardment by heavy ions. The structure of the atomic bonding in this film turns out to be extremely disordered and represents a mixture of sp^1 , sp^2 , and sp^3 hybridizations. Due to the high content of bonds with the sp^3 hybridization, such a film acquires diamond-like properties. The tetrahedral film is characterized by high hardness and wear resistance, which makes it possible, in view of the

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optical transparency of such a film, to use it as a protective coating for optical fibers. Owing to the high cohesion energy and large activation energy, carbon polymorphism exists in a wide range of metastable states. Graphite compressed along the *c*-axis under a pressure of 10 to 25 GPa at room temperature is able to retain the strongly compressed structure. However, upon heating under high pressure, graphite passes into a diamond cubic structure. The authors of [2–8] have supposed that the strong compression gives a new superhard phase of carbon. Indeed, at pressures between 10 and 25 GPa, an increase was observed in the resistance [2] and in the optical transparency [3, 4], and there was a decrease in the optical reflectance [5] and changes in the X-ray diffraction patterns [6–8]. Several hypothetical structures have been suggested to explain these features; for example, sp^2-sp^3 graphite–diamond structures [9], M carbon [10], body-centered tetragonal (bct- C_4) carbon [11], and W carbon [12]. However, all these models have proved to be unable to reflect the complete spectrum of experimental data. The problem of the existence of a superhard phase of carbon remains disputable. Apparently, a phase transformation indeed takes place, since, upon a further increase in pressure to 40 GPa or more, the compressed carbon is transformed into amorphous carbon; this follows from its Raman spectra (RSs) [13].

Purely carbon molecules — C_{60} and C_{70} fullerenes — were also discovered. Later, carbon tubes and, finally, graphene have been obtained.

In 2010, A Geim and K Novoselov won the Nobel Prize in physics for experiments performed with graphene, in which they showed its unusual properties explained by quantum physics. The energy-band structure of ideal graphene is unique, since no energy gap appears in it. In six Dirac K points, the zone with positive values of energy corresponding to electron states, touches the zone with the negative energy that characterizes hole states. Near these points, the energy spectrum acquires a linear dependence on the wave vector. According to the characteristics of the energy bands, graphene, depending on the conditions and impurities, can be a metal or a semiconductor. Graphene is an extremely good conductor of electricity and heat. It is the strongest of all two-dimensional media and, at the same time, is sufficiently plastic. It is almost completely impenetrable and almost completely transparent to light. Owing to these characteristics, graphene finds very wide application.

The main experimental method for the investigation of the mechanical properties of graphene or pieces of multilayer graphene (stacks of graphene layers) is atomic-force microscopy (AFM). In [14], AFM was used to study the elastic properties of a stack of graphene layers (fewer than five) on a substrate of silicon dioxide. The Young's modulus of the graphene stack was about 0.5 TPa. An analogous experiment was performed using a graphene monolayer [15] to obtain a Young's modulus of about 1 TPa.

The elastic properties of diamond have been studied experimentally much better than those of graphene, but even for diamond the spread of the data is rather substantial (0.41–0.59 TPa). The elastic properties of diamond were apparently first measured in 1946 with the use of ultrasonic methods [16, 17]. Later, they were also measured by X-ray diffraction and precise acoustic methods [18–20].

The mechanical and optical properties of materials depend on their dimensions and shape. For example, single-crystal fibers have substantially higher hardness and ultimate

strength than those of loose materials in view of the absence of growth defects in such fibers. Information on the various mechanical properties of carbon nanotubes, fullerenes, and other closed carbon structures (nanotubulens: capsulens, torens, barrelens, etc.), as well as on the methods of their preparation and on the behavior of carbon during the formation of condensed phases are given in reviews [21–24] (see also [25, 26]).

In this review, we restrict ourselves to the consideration of the mechanical properties of graphene, partly discuss the influence of defects on its properties, and present the results of investigations of the structure and of the edges of graphene, its resistance to heating and deformations of uniaxial tension and compression. In addition, we present the results of recent investigations of the thermal stability of graphene coated with a metallic film. As a rule, theoretical and calculated investigations were based (where possible) on the experimental data.

2. Transformation of graphene under the effect of mechanical and chemical actions

2.1 Preparation of tubes and scrolls of graphene

Graphene possesses a rather flexible and mobile structure and has a tendency to acquire a three-dimensional form under certain external conditions. In this case, a minimization of the surface energy occurs [27]. If the ratio of the length of the graphene sample to its width is sufficiently large (narrow graphene ribbon), such a structure spontaneously begins self-folding [28]. During self-folding, the graphene ribbons can form multilayer spiral structures [29, 30] of different diameters [31, 32]. The factors that are responsible for the processes of scrolling, bending, and rotations of graphene can be low-temperature ($T < 100$ K) fluctuations [33] and the internal instability of the structure [34].

There are investigations devoted to the transformation of graphene ribbons into nanotubes via confined polymerization of polycyclic aromatic hydrocarbons (PAHs) [35, 36]. Experimentally, graphene tubes are produced by scrolling a graphene ribbon located inside a carbon tube of greater diameter [37]. In this case internal tubes with the desired chirality can be obtained. The theoretical model developed in [38] suggests that the graphene ribbons located inside a nanotube of a large diameter will form spiral structures because of the external geometrical confinements. The same conclusion follows from quantum-chemical simulations [37], according to which a graphene ribbon completely located in a nanotube will spontaneously twist into a spiral. The process of twisting is initiated by the formation of bonds between the surface of the tube and edges of the ribbon. In this case, a torque arises. The twisting continues until the formation of a completed tube. The properties of a defect-free carbon tube obtained from graphene under the action of tension were analyzed in terms of a molecular-dynamics (MD) model [39]. As the angle of chirality increased, a monotonic increase in the tensile force and deformation of failure was observed.

Graphene scrolls, unlike nanotubes, have a topologically open structure, which, along with the unique mechanical and electromechanical properties of scrolls inherited from the graphene sheet [40, 41], opens wide opportunities for their application. The scrolls can be applied as a medium for storage of hydrogen [42], as water and ionic channels [43], and as nanosolenoids [44].

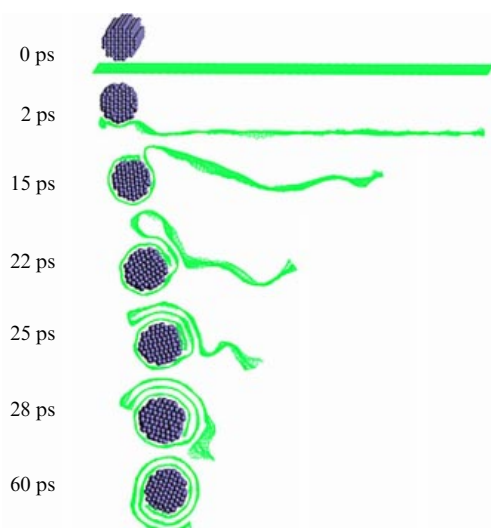


Figure 1. Dynamics of spontaneous scrolling of a graphene ribbon around an Fe nanowire [27].

However, the scrolling of an isolated graphene sheet is a quite difficult problem. Its internal energy of elasticity, which is always directed towards the retention of the flat shape, creates an energy barrier to the structural transition. And the scrolling becomes possible only if a nanorod, e.g., made of iron, is introduced into the system (Fig. 1) [27]. The van der Waals interaction between the graphene and the iron nanorod helps overcome the energy barrier and creates a force of attraction, which leads to contact between the iron rod and the graphene ribbon in the process of scrolling. In this case, a three-dimensional core–multilayer-shell structure is formed. If the rod is initially located in the middle of the ribbon [45], the scrolling results in the formation of a nodular structure with double walls. If two nickel nanorods are placed at the different ends of the ribbon, a dumbbell-like structure is obtained. According to [27, 45], the process of scrolling of graphene on a metallic rod is irreversible. This, according to the authors of [27, 45], suggests the metastability of graphene.

A scrolled graphene structure can be obtained by chemical methods [46]. The structure of carbon scrolls with different diameters and chiralities was investigated experimentally, depending on the dimensions of the sheet and direction of scrolling [47, 48]. The scrolling of graphene was also studied using MD simulation in [49, 50], where the scrolling was initiated by a carbon nanotube with the formation of a tube/scroll–core/shell composite (Fig. 2). The character of this process is determined by the tube–graphene and graphene–graphene interaction energies. The success of the formation process for a scroll mainly depends on the diameter d of the tube. The tube can help graphene to overcome the energy barrier only when d is relatively large. Such a structure remains stable for at least 500 ps at $T = 300$ K. Because of the strong adhesion between the graphene and the tube, it is fairly difficult to separate such a structure into its initial components.

The controlled doping by hydrogen makes it possible to obtain graphene with easily tuned properties [51]. Via the addition of hydrogen atoms to carbon, the sp^2 structure of the graphene sheet is replaced by an sp^3 structure. In other words, the two-dimensional atomic structure of pure graphene passes into a local three-dimensional structure around each

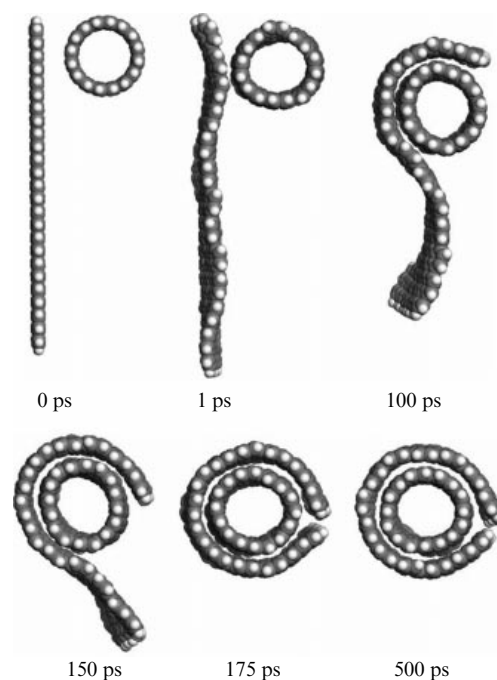


Figure 2. Spontaneous scrolling of a graphene ribbon around a carbon nanotube [49].

absorbed hydrogen atom [52]. Such structures can be obtained both on the macroscopic scale and on the micro-scale [53].

In [54], the possibility of the spontaneous scrolling of a quadratic graphene sheet partly doped with hydrogen has been studied using MD calculations. Depending on the ratio between the length L_H of the region enriched in hydrogen atoms and its width W_H , three different results can be obtained: partial scrolling of the hydrogen-containing part of graphene; complete scrolling of the entire sheet; or an irregular nanostructure. The last appears as a result of scrolling produced from three sides. A graphene sheet doped with hydrogen forms a scroll, which is stable at $T = 300$ K if the following relationship is fulfilled: $0.4 \leq L_H/W_H \leq 0.6$ (Fig. 3) [54].

Graphene platelets with different shapes with a significant van der Waals interaction between the layers can also spontaneously form large bulk structures [55, 56]. Separate platelets (graphene flakes) with a high plasticity can be twisted into nanoscrolls under the effect of certain gases and alcohols [57, 58].

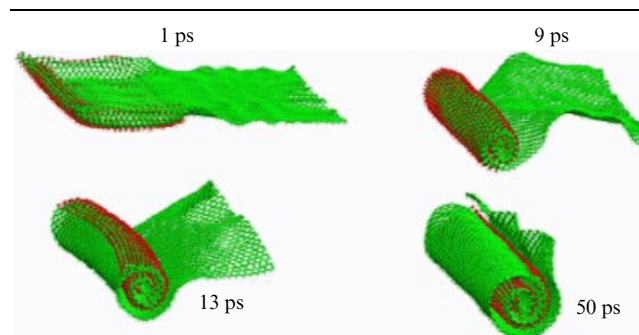


Figure 3. Complete scrolling of a graphene sheet partly doped with hydrogen ($L_H/W_H = 0.4$) [54].

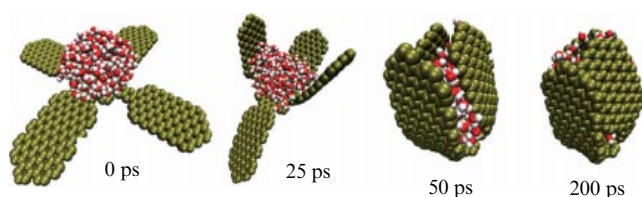


Figure 4. Scrolling dynamics of rectangular graphene sheets interacting with a nanodroplet of water [59].

The folding of four graphene platelets that interact with a water nanodroplet has been studied based on the MD model in [59] (Fig. 4). After a certain time (50 ps), the graphene lobes closed completely. In this case, a nanocapsule containing water molecules inside was formed. The energies (determined in *ab initio* calculations [59]) of the initial (open) and final (closed) structures with water molecules inside are equal to -150.3 and -913.56 kJ mol $^{-1}$, respectively. This characterizes the water-graphene scroll as a more stable formation than a water nanodroplet with open lobes [59]. In the presence of an SiO $_2$ substrate, the strong interaction between the graphene lobes and the substrate prevented the formation of a closed structure of graphene. In addition, SiO $_2$ is more hydrophilic than graphene. For this reason, the expanding water nanodroplet, which tends to cover the surface of SiO $_2$, prevents the folding of graphene. However, when there is a layer of isopropyl alcohol between the graphene and the substrate, the alcohol molecules shield the strong interaction between graphene and SiO $_2$. The interaction between graphene and water in this case is not weakened. This permits the graphene lobes to close. The governing parameters in the formation of a bulk structure in this case are the geometry of the flat graphene structure and the dimensions of the water nanodroplet and substrate.

The scrolling of graphene was also obtained based on an MD simulation of two rectangular plates connected by a narrow graphene ribbon at the center of which a water nanodroplet was placed [60]. After 250 ps (at $T = 300$ K), the plates folded into a bulk structure with a water droplet inside. When the temperature increased to $T = 400$ K, the mobility of the water droplet increased, the plates contracted, and the water molecules were squeezed outside, remaining on the surface. The shape of the scroll could be controlled by changing the size of the droplet. When the droplet contained 10,000 molecules, the ribbon, while scrolling, formed a multilayer structure similar to a multiwall nanotube filled with water.

Thus, the computer experiment showed the ability of a water droplet to activate and guide the process of graphene folding into one of the bulk nanostructures: capsule, knot, ring, or layered [60].

2.2 Transformation of graphene into fullerene

Graphene is an ideal structure for the formation of fullerene, which consists of a finite number of sp 2 -hybridized carbon atoms and does not have open edges. The graphene-fullerene transformation has been demonstrated using the MD model in [61, 62]. At temperatures of 3000–3500 K, the folding of a graphene film (100–700 atoms) into fullerene occurs in several nanoseconds. The formation of the C $_{60}$ and C $_{70}$ structures from graphite in a vacuum has been experimentally observed by stimulation with an electron beam with an energy of 10 keV [63].

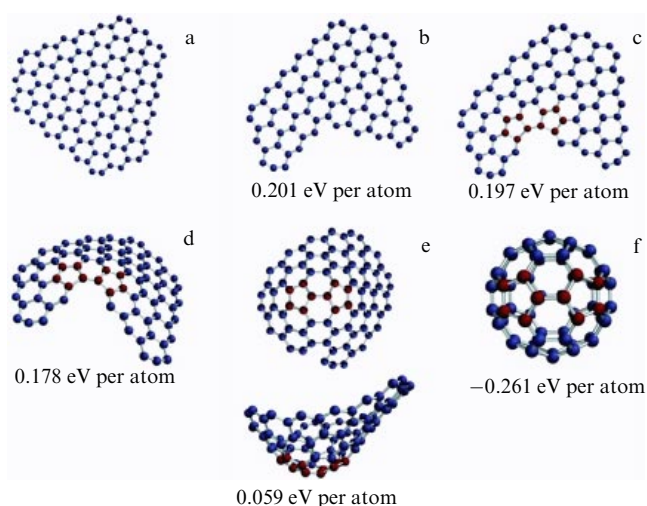


Figure 5. Stages of the process of the formation of fullerene from a graphene platelet [64].

It has been shown in [64] that under the action of an electron beam with higher energy (80 keV), the graphene sheet can acquire a spherical shape. The high energy of a beam leads to the fragmentation of large regions of graphene into small flake-like structures. In the final analysis, fullerenes are formed from these structures. The loss of carbon atoms from the graphene edges is a key event in the process of the formation of fullerene [65, 66]. The action of a high-energy electron beam destabilizes the edge structure of graphene because of the loss of atoms from the edges and the appearance of a large number of dangling bonds.

The process of the transformation of graphene into fullerene can be studied in detail based on the quantum-chemical model developed in [64] (Fig. 5). The formation of pentagonal rings at the edges and the subsequent folding of the platelet are energetically favorable processes. The atoms of carbon with lacking bonds are brought to one another; thereby, the formation of new C–C bonds is initiated between them. The newly formed bonds lead to the folding of the edges, creating a stabilizing effect (Fig. 5d). Such a cap-like structure can continue folding, losing carbon atoms, and pentagons are formed in this structure. The folding continues until the finished structure is formed.

Note that for the full folding of graphene into fullerene, the initial size of the graphene platelet is of large importance. If the plate is too large, significant energy will be spent on removing the edges. The etching of the edges stops only when, during the formation of the fullerene, the platelet reaches a certain size specified by the thermodynamic conditions of chemical equilibrium. However, if the platelet is too small (less than 60 carbon atoms), then upon folding a strong tension of C–C bonds will occur, which can lead to the destruction of the pentagonal rings. The number of carbon atoms that is needed for the optimal formation of fullerene is 60–100.

One more factor that can act on graphene during the formation of fullerene is temperature [67]. MD calculations have shown that the transformation of graphene into a fullerene under the action of a temperature of 2700–3500 K starts with the breaking of the C–C bonds located nearest to the edge of the graphene sheet. The gradual rearrangement of the edge structure continues until the planar sheet containing 96 or 384 carbon atoms begins transforming into a cap. In

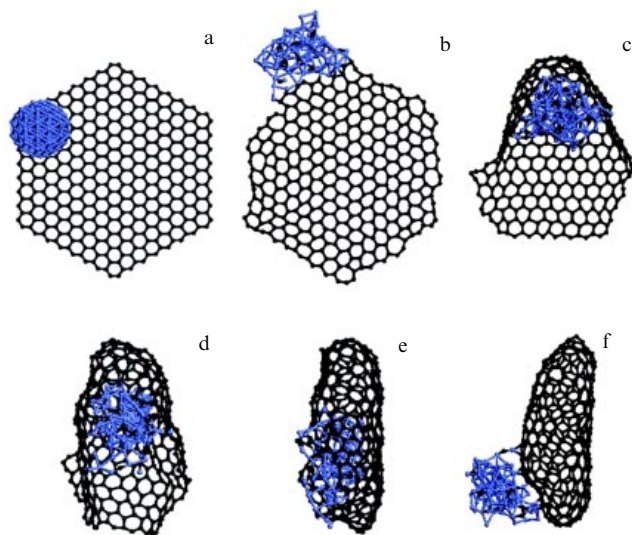


Figure 6. Structures obtained as a result of MD simulation of the transformation of a graphene sheet C_{384} into fullerene in the presence of an Ni_{79} cluster at $T = 2500$ K at various time moments: (a) 0; (b) 3; (c) 6.6; (d) 6.8; (e) 7.0; and (f) 11.5 ns [67].

such a structure, locking of the edges occurs rather rapidly with the formation of a closed structure, i.e., fullerene. The energy of activation for this process is about 4 eV. At $T = 2500$ K, the average time of folding for graphene C_{384} is 3–4 times that for graphene C_{96} .

Clusters of Ni atoms can serve as a catalytic driving force for this process (Fig. 6) [67]. Modern technology makes it possible to prepare a metallic cluster consisting of a certain number of atoms (including atoms of different elements) and to place it onto a graphene sheet of a desired size [68]. In the presence of an Ni cluster (containing 13 or 79 atoms, depending on the size of the graphene sheet), the temperature of scrolling decreases to 2000–3000 K. The cluster moves along the edge of the graphene sheet via the diffusion transfer of carbon atoms onto the cluster and back. This process continues until graphene is transformed into a cap-like structure and is closed around the cluster. In this case, the Ni cluster can either remain inside the fullerene shell or escape from it. The energy of activation for this process for the $C_{384} + Ni_{79}$ system is 1.5 eV, which is significantly less than that in the absence of the catalyst on the graphene surface.

3. Mechanical properties of graphene, its resistance to deformation by tension and compression

3.1 Changes in the electronic properties of graphene upon lattice deformation

Graphene is a very strong and easily distensible material. Along with other mechanical properties of graphene, its resistance to elastic deformations has been studied. The creation of elastic deformations is considered as a promising method of modifying the properties of nanomaterials [69]. A significant change in the interatomic spacings and in the symmetry of the crystal lattice under large elastic deformations can lead to the appearance of unusual mechanical, thermal, optical, electrical, magnetic, and other properties of materials. For example, the thermal conductivity of graphene

and carbon nanotubes decreases monotonically with increasing tensile stress [70, 71]. The optical conductivity of graphene is also very sensitive to applied stress [72, 73]. A uniaxial stress leads to a red shift of the G line (splitting it into two) and of the 2D line in the spectrum of Raman scattering from graphene¹ [74].

The electronic properties of graphene depend on its two-dimensional structure and on the structure of its full symmetry. The lattice consists of two triangle sublattices; therefore, the electron spectrum of graphene is characterized by two branches, which touch each other at the so-called Dirac points, i.e., at two nonequivalent points K and K' located at the corners of the hexagonal first Brillouin zone.²

One of the key problems is the effect of impurities on the electronic properties of graphene [75]; the understanding of these effects is important for further technological development. One more way to modify the electronic properties is the creation of stresses in the lattice. The presence of deformations can exert a significant influence on the operation of electronic devices.

Graphene, because of its low dimensionality, has remarkable mechanical properties. In particular, *ab initio* calculations and experiments have shown that significant (up to 20%) elastic stresses can exist in single-layer graphene [76, 77]. The uniaxial deformation initiates a modification of electronic branches and, consequently, collective electron excitations (plasmons) [78]. The effects of the local fields make it possible to include into the consideration all processes of scattering with an arbitrarily low wavelength, i.e., to take into account the discrete nature of the crystal lattice. The contraction of the valence branch and of the conduction branch of graphene induced by the uniaxial deformation of the lattice has been considered in [78].

3.2 Strength of graphene under tension and the mechanism of its fracture

In [79], a simulation of the uniaxial extension of graphene along different chiral directions was performed in the MD model with the use of a reactive empirical bond order (REBO) potential of interatomic interaction [80]. The chiral direction was in the range of angles $0 < \alpha < 30^\circ$; for the 'zigzag' direction, $\alpha = 0$, the step of deformation $\Delta\epsilon = 0.002$. The increasing dependences of the potential energy of lattice stresses on the deformation exhibit a sharp falloff corresponding to the breaking of the graphene sheet. With increasing angle α , the falloff of the stress is shifted towards the smaller values of ϵ .

The dependence of the limiting deformation and stress on the chiral angle α is shown in Fig. 7. The breaking deformation changes significantly (from 0.178 to 0.283), whereas the change in the breaking stress is not so large (from 30.5 to 35.6 N m⁻¹). The maximum values of the fracture parameters are achieved in the zigzag direction ($\alpha = 0$); the minimum values are in the 'armchair' direction ($\alpha = 30^\circ$). The experimentally established values of these parameters (0.25 and 42 N m⁻¹, respectively) have been obtained for suspended graphene sheets in the case of isotropic deformation [81].

¹ The origin of these lines is explained in Section 3.4.

² The Brillouin zone is defined as the transform of the Wigner–Seitz cell of the crystal in the reciprocal space. Certain points of high symmetry in the Brillouin zone are denoted by special symbols.

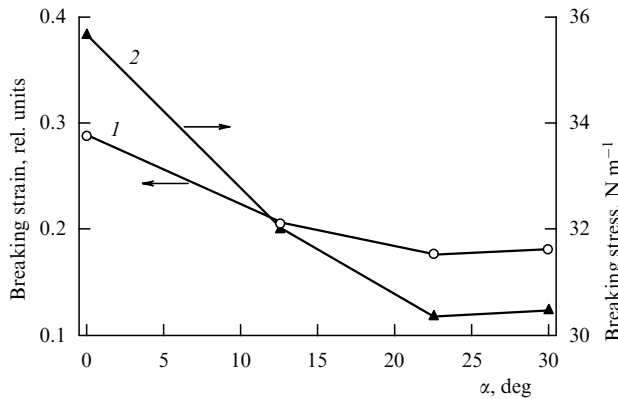


Figure 7. Deformation (1) and stress (2) that break graphene sheets under the action of tensile stress along different chiral directions [79].

A rougher simulation of the fracture of graphene upon uniaxial extension was performed with the use of elements of quantum-chemical calculation [82], in which the force of deformation F_i was determined as the gradient of the total energy of the system along the mechanochemical i th coordinate. A system of 88 atoms was studied with a step of deformation $\Delta\epsilon = 0.008-0.009$. One of the ends of the object was fixed rigidly; the opposite end could move. The extension was performed in both zigzag and armchair-type directions. The final deformation was calculated with the use of a linear relation between F and ϵ , which was established via Hooke's law. In both cases, the same value of the fracture deformation was obtained, $\epsilon_{cr} = 0.123$, which is significantly less than the limiting values of ϵ determined in [79, 81]. The ratio between the values of the breaking stresses in the zigzag and armchair directions also diverged strongly: 1.53 [82] and 1.16 [79].

The fracture of the material occurs most frequently because of the formation and development of cracks. Precisely such an approach was demonstrated in [83], where the growth of cracks is considered in a discrete atomic model of graphene, as opposed to the continuum-mechanics approach. The model included 728 carbon atoms, the interaction between which is described by the Tersoff–Brenner potential [84]. The calculations were performed for the case of cracks with infinite and finite lengths. The formation of a crack was initiated by the breaking of bonds between the chains of atoms. The coefficient W of the liberation of the energy of elastic deformation was calculated in two ways. The first was the method of global energy, which is based on the determination of the total potential energy of two graphene sheets with different lengths of the central cracks ($2a$ and $2a + 2\Delta a$), so that the coefficient W was written as follows:

$$W = -\frac{U_{2a+2\Delta a} - U_{2a}}{2\Delta ah}, \quad (1)$$

where U_{2a} and $U_{2a+2\Delta a}$ are the total potential energies of the graphene sheets in the deformed states obtained in the discrete atomic model; Δa is the equilibrium interatomic spacing in the x direction (along the crack); and h is the thickness of the graphene sheet.

In the second method—the method of local force—the virtual work which is required to prevent crack propagation is determined. Here, one should not calculate the total potential energy. This method is the fastest one and can be applied to

Table 1. Coefficients W/σ_0^2 determined in the model of graphene with a crack of infinite length [83].

Length, nm	$W/\sigma_0^2, 10^{-20} \text{ J Pa}^{-2}$, for a crack in graphene		
	Atomistic simulation		LEMF
	Method of global energy	Method of local force	
1.005	0.259	0.252	0.283
2.009	0.498	0.482	0.510
3.014	0.753	0.726	0.769
4.018	1.029	0.992	1.037
5.023	1.342	1.294	1.354
6.027	1.708	1.647	1.688

large atomic systems, since only neighboring atoms near the tip of the crack are taken into account in the calculations. In this case, the mechanism of fracture can be presented by two main deformation modes: I and II. The tensile mode I describes the relative displacements between the atomic pairs whose atoms are located symmetrically relative to the normal to the crack surface. The sliding mode II reflects sliding by making antisymmetrical separation of atoms via tangential (with respect to the crack surface) displacements. The linear elastic solution (u_x, u_y) for the displacement fields in the vicinity of the crack tip in the case of modes I and II is given in [83]. The coefficients of energy liberation W_I and W_{II} for modes I and II are written as follows:

$$W_I = \frac{1}{2\Delta ah} F_y(v^+ - v^-), \quad (2)$$

$$W_{II} = \frac{1}{2\Delta ah} [F_x(u^+ - u^-) + F_y(v^+ - v^-)], \quad (3)$$

where F_x and F_y are the interatomic forces acting on the i th atom in the x and y directions, respectively, from the side of atoms located near a crack $2a$ long; and u^+, u^-, v^+ , and v^- are the displacements that open the crack in the x and y directions for the i th and j th atoms located in the vicinity of a crack $2a + 2\Delta a$ long. In order to obtain the value of the virtual work, it is necessary to perform calculations with the use of two configurations. The first one restores, the deformation of the crack expansion, while the second one—the shift along the crack.

For example, Table 1 contains the values of the fracture parameters for a crack of infinite length. Good agreement can be seen between the values of W/σ_0^2 determined by the first and second methods. Here, $\sigma_0 = F_0/A$, where F_0 is the external force (calculated from the displacements specified by the network) applied to the system, and A is the area of the transverse section of the graphene sheet. In addition, the parameter W/σ_0^2 calculated in terms of the discrete atomic model agrees with the analogous quantity determined via the method of linear elastic mechanics of fracture (LEMF). This shows that the LEMF is applicable for the description of the propagation of cracks in covalent-bonded nanomaterials, and that the atomistic approach yields adequate information on the mechanisms of their fracture.

The Young's modulus Y of graphene was measured using the AFM. Graphene was subjected to an external deformation and the relationship between the force and displacement was written systematically [81]. The Young's modulus measured in this experiment was equal to 1.0 ± 0.1 TPa. The usual method of measuring Y is the determination of

the slope of the dependence of the stress on the deformation that creates this stress [85–87]. The Young's modulus of carbon nanotubes (CNTs) was also determined mainly in this way. However, in the experiments performed in [88], another approach was applied: the magnitude of Y was established from the observation of thermal vibrations near the tip of a CNT using a transmission electron microscope (TEM). For an unknown reason, this method was not employed to determine the Young's modulus in graphene. The magnitude of Y for graphene was obtained by the investigation of thermal fluctuations in the MD calculation [89] with an REBO interatomic potential [80]. The average square of the displacement (ASD) of atoms in graphene is connected with the acoustic phonon mode, which has a parabolic dispersion law $\omega = \beta k^2$.

Suppose that a graphene sheet with a square shape with a side L forms a plane xy . Then, the equation for the vibrations in the z direction acquires the form [90]

$$\rho \frac{\partial^2 z}{\partial t^2} + \frac{Q}{h} \Delta^2 z = 0, \quad (4)$$

where $Q = (1/12) Y h^3 / (1 - \mu^2)$; Δ is the two-dimensional Laplacian; ρ is the graphene density; μ is Poisson's ratio; and h is the thickness of the graphene sheet.

The solution to Eqn (4) with fixed boundary conditions in the x direction and periodic boundary conditions in the y direction has the following form:

$$\omega_n = k_n^2 \sqrt{\frac{Y h^2}{12 \rho (1 - \mu^2)}},$$

$$z_n(t, x, y) = u_n \sin(k_1 x) \cos(k_2 y) \cos(\omega_n t), \quad (5)$$

where $k_1 = \pi n_1 / L$, $k_2 = 2\pi n_2 / L$, $\mathbf{k} = k_1 \mathbf{e}_x + k_2 \mathbf{e}_y$, and $\mathbf{e}_x$ and $\mathbf{e}_y$ are the basis unit vectors.

Using these eigenvalues for an ASD of the n th mode of the phonon in the (x, y) plane, we obtain [91]

$$r_n^2(x, y) = 4k_B T \frac{12(1 - \mu^2)}{Y h^3 L^2} \frac{1}{k_n^4} [\sin(k_1 x) \cos(k_2 y)]^2. \quad (6)$$

Under the conditions of thermal equilibrium at a temperature T , all the modes are independent and make a noncoherent contribution to the ASD. Therefore, we can obtain the following simplified expression for the ASD [89]:

$$\langle r^2 \rangle = \sum_{n=0}^{\infty} \langle r_n^2 \rangle = 0.31 \frac{(1 - \mu^2) L^2}{h^3} \frac{k_B T}{Y}. \quad (7)$$

Hence, assuming that $\mu = 0.17$ for graphene [92, 93], we have

$$Y = 0.3 \frac{L^2}{h^3} \frac{k_B T}{\langle r^2 \rangle}. \quad (8)$$

Using Eqn (8), the authors of [89] obtained the dimension dependence of Y for a square graphene sheet. The magnitude of Y increases from 0.7 to 1.1 TPa as the edge of the graphene sheet increases from 1 to 4 nm and is retained with small fluctuations during a further increase in the dimension of the sheet. In the temperature range of 100–500 K, a 15% increase in Y is observed. However, at $T > 500$ K, a rapid decrease in Y occurs, which is related to a significant increase in the ASD in the z direction and, consequently, to an increase in the total

ASD. According to the authors of [89], this method of determining Y gives correct values of the Young's modulus only in the temperature range of $100 \leq T \leq 500$ K. The authors of [89] also studied the effect of the isotopic composition of graphene on the value of the modulus Y . To this end, atoms of isotope ^{14}C were introduced randomly into a pure ^{12}C system. It was shown that while the concentration of ^{14}C is no more than 5%, the modulus Y changes in narrow limits ($1.05 < Y < 1.1$ TPa). However, when the concentration of ^{14}C increases to 20%, the value of Y decreases by 15%. Such a behavior of Y is opposite to the behavior of thermal conductivity of graphene upon a change in its isotopic composition. Thus, upon an isotopic disorder of 5%, the thermal conductivity of graphene could decrease up to 40% [94, 95], whereas a further increase in the concentration of ^{14}C did not lead to substantial changes in the thermal conductivity.

3.3 Stability of graphene under the effect of compressive deformations

Based on the results of MD simulation, the strong plastic deformation of compression in the zigzag and armchair directions of a free-standing graphene sheet has been studied [96]. A fundamentally different behavior of the graphene sheet was revealed when these deformations were present. The compression along the zigzag direction weakens the edges of the sheet parallel to this direction because of the local destruction of the cellular hexagonal structure along the lower and upper edges of the sheet. In the final account, after the implementation of 59 acts of compression through $\varepsilon = 0.0058$, the graphene sheet retained its integrity, losing only a small number of C atoms (Fig. 8a). The defect cellular hexagonal structure was retained in the H form. Along the armchair direction, the graphene sheet is unable to sustain such strong stresses of compression.

Under the effect of compression along the zigzag direction, the C atoms begin to escape from the sheet in the vertical direction (along the z -axis) already under relative deformations $\varepsilon = 0.0235$, and upon compression along the armchair direction, at $\varepsilon = 0.0266$. A further compression of the sheet leads to an increase in the number of atomic displacements in the z direction. In addition, the paths passed by the atoms in this direction increase.

The compression of a graphene sheet in the armchair direction already at moderate deformations creates cracks along the zigzag direction. Then, because of these cracks,

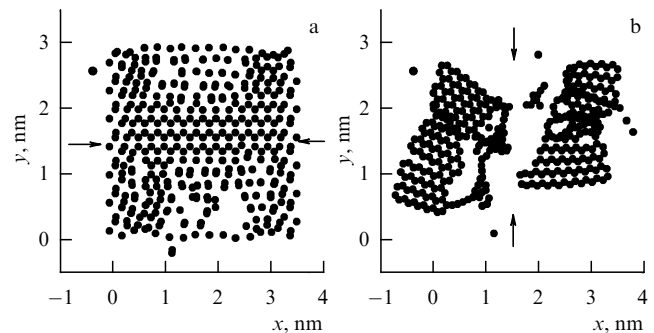


Figure 8. Projection of a graphene sheet onto the plane xy upon its compression along the direction of (a) zigzag and (b) armchair types at relative compressive deformations 0.3469 and 0.3929, respectively. The arrows indicate the direction of deformation [96].

wavy channels arise in the armchair direction; separate fragments of the graphene sheet rotate and shift. In this case, a widening of one of the arising channels is observed. The rotated left-hand and right-hand parts of the sheet slide along this channel; as a result, the sheet becomes completely broken (Fig. 8b). The difference in the stresses of the atomic rows of the graphene sheet in this case is an order of magnitude less than in the case of compression of the sheet along the zigzag direction.

3.4 Investigation of deformations using the Raman spectroscopy method

In applications of single-layer graphene, its response to various loads is of great importance. The work in this field is mainly theoretical. Experimental investigations, as a rule, are limited to the study of bending of separate graphene flakes in air or of tensile tests until a certain deformation ($\approx 1\%$) with the use of plastic substrates. Using a cantilever geometry, single-layer graphene can be subjected to axial compression to different degrees. The resistance of graphene flakes of different geometries to compression has been studied in [97]. In all the cases, the mechanical response was controlled by the shift of the G or 2D phonons of graphene in the spectrum of Raman scattering. The results show that graphene mounted into a plastic beam demonstrates compression on the order of 0.5–0.7% and sometimes more than 1%.

One of the methods for recognizing to what extent the material is able to sustain the applied stresses or deformations is the investigation of its phonon frequencies under a load. Raman spectroscopy is a very successful tool for the monitoring of phonons for a wide class of materials subjected to the action of a uniaxial stress [98] or hydrostatic pressure [99]. Under the effect of a tensile load, a softening of phonons is observed; under the effects of compression, on the contrary, their hardening occurs. In general, in graphite materials (such as polycrystalline CF) the final deformation is affected not only by tensile (compressive) stresses but also by some mechanisms of rotation and sliding of crystallites that do not change the phonon frequency [98].

The recently developed method of obtaining graphene via the mechanical splitting of graphite [100] makes it possible to study the Raman shifts of the bands of both the G and 2D modes [101] under the tensile or compressive load on a molecular level [102–104]. This is important not only for the detection of superstrength and rigidity of graphene, but also to relate its behavior to the mechanical deformation of other graphite structures, such as bulk graphite, carbon nanotubes, and CFs. The G peak corresponds to the double degeneracy of the E_{2g} phonon in the center of the Brillouin zone. The D peak, which is due to the ‘breathing’ modes of sp^2 -bonded rings, requires the presence of a defect for its activation [101, 103]. This peak, which is due to transverse optical phonons near the K point of the Brillouin zone [99, 105], is activated by a double resonance [106] and has a strong dispersion at the point K [107]. The 2D peak, which is a second-order feature that is formed from the D peak, is the only peak in monolayer graphene; already in two-layer graphene, it is split into four peaks, reflecting thereby the evolution of the band structure [101]. Since the 2D peak appears in the process in which the moment is retained because of the participation of two phonons with opposite wave vectors, it does not require the presence of defects for its activation and, therefore, always exists. Indeed, in high-quality multilayer graphene, the G and 2D peaks exist but the D peak is absent [101]. A large number

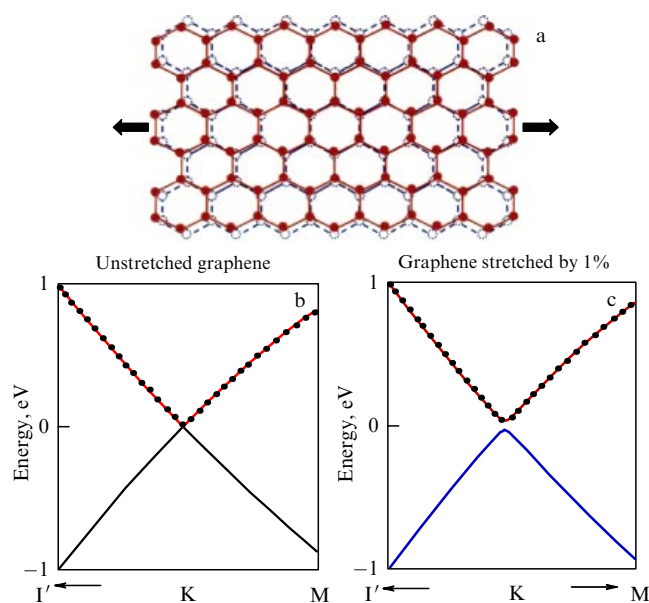


Figure 9. (a) Effect of uniaxial tensile deformation on a graphene piece (schematic). The deformed lattice is shown by solid lines; the undeformed initial lattice by dashed lines. (b) The band structure of the undeformed graphene calculated along the I' -K-M direction of the Brillouin zone. (c) Same as in Fig. 9b, but for graphene with 1% deformation. In the band structure of stretched graphene, the appearance of a band gap can be seen [112].

of studies are available in which the behavior of these peaks was studied under the application of deformations of different magnitudes to graphene [102–104, 108].

Because of the thin single-layer structure of graphene, the uniaxial deformation can strongly change its electron and optical properties. Since graphene has two carbon sublattices which behave differently upon uniaxial deformation, it is possible to control the band gap by breaking the symmetry of the sublattices [109–111].

For example, the opening of a band gap was predicted in [111] for the growth of graphene on a hexagonal substrate of boron nitride because of the violation of the equivalency of the sublattices. In [112], graphene sheets deposited onto a flexible polyethylene substrate were subjected to uniaxial tension (with a deformation up to $\approx 0.8\%$). To study the effect of deformation on single-layer and three-layer graphene, Raman scattering has been used. Significant red shifts of the 2D peak (-27.8 cm^{-1} per percent of deformation) and G peak (-14.2 cm^{-1} per percent of deformation) were observed for single-layer graphene under the action of uniaxial tensile deformation. The results of a simulation based on the density-functional theory (DFT) have shown that in this case an opening of a band gap (300 meV at a 1% deformation) occurs at the K point of the Brillouin zone (Fig. 9). This effect can be used to fabricate various devices based on the application of the graphene properties.

3.5 Effect of defects on the mechanical properties of graphene

Let us now consider defects in graphene in the form of nitrogen atoms implanted into vacancies and rising above the graphene surface [113]. The initial sheet of graphene contained 588 atoms. The covalent C–C bonds were formed using the REBO potential [80]; the C–N bonds were formed

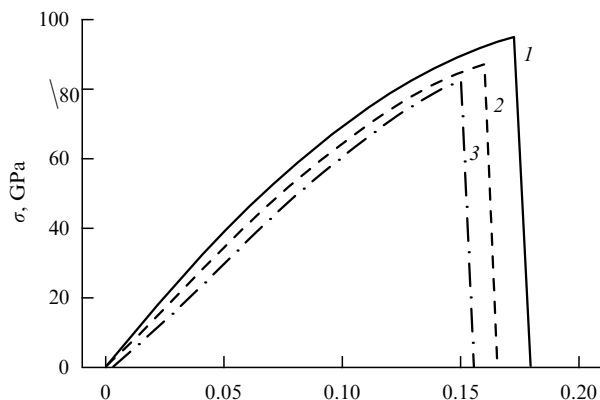


Figure 10. Stress–strain curves for graphene containing uniformly distributed nitrogen atoms in the amounts of (1) 0, (2) 1, and (3) 4% [113].

using the Tersoff potential [68, 114]. The N atoms were placed into the vacancies both in a regular way and randomly. The Young's moduli were determined from the slopes of the linear segments of the dependences of stresses on the tensile deformation $\sigma(\varepsilon)$ constructed using a step $\Delta\varepsilon = 0.004$. The stresses created by the forces applied in the zigzag direction always decreased sharply when the deformation reached the critical value close to the fracture of the graphene sheet.

Figure 10 shows examples of some stress–strain curves for graphene containing uniformly distributed nitrogen atoms. The calculated limiting tensile stresses and Young's moduli for the cases of a regular and random placement of N atoms are given in Table 2. These characteristics change only moderately with changing nitrogen content. In the case of a random distribution of nitrogen atoms over the vacancies in graphene, observed is, as a rule, a greater decrease in the magnitude of the limiting deformation (as compared to that for pure graphene) and in the ultimate strength (as compared to that corresponding to the uniform distribution of nitrogen atoms). The values of the Young's modulus only weakly depend on the changes in the nitrogen content.

When only two nitrogen atoms have been implanted, it has been shown that the ultimate strength decreases with decreasing spacing between them. When the spacing between N atoms was 0.176 nm, the ultimate strength decreased by 25%. The maximum stress arose near C atoms neighboring N atoms; i.e., in the vicinity of nitrogen atoms, it was the C–C bonds that became broken rather than the stronger C–N bonds.

Table 2. Mechanical properties of graphene containing uniformly (regularly) and randomly distributed nitrogen atoms [113].

Nitrogen content, %	Ultimate strength, GPa	Young's modulus, GPa
Regular distribution of nitrogen atoms		
0	94	786
1	88	758
2	87	774
4	84	772
Random distribution of nitrogen atoms		
1	82	766
2	70	809
4	86	840

The experimental value of the relative deformation of the longitudinal compression for graphene ribbon on a substrate is, as a rule, 0.5–0.7% [115, 116]. At such a deformation, sinusoidal waves (buckling) are revealed on the graphene ribbon. The roughness of graphene suspended in a vacuum appears at substantially lower deformations [115]. In [117], the MD method was used to study the behavior of a compressed single-layer graphene platelet on a substrate in the presence of randomly distributed vacancies. In the presence of vacancies, buckling on the compressed platelet appeared at smaller deformations; the decrease in the buckling strain threshold obeyed a linear dependence. In the absence of vacancies, the nonlinearity of the stress–strain curve manifested itself at approximately the same strains as the buckling on the plate. The magnitude of the deformation corresponding to the loss of stability ($\sim 0.6\%$) agrees with the corresponding experimental characteristic.

4. Ion beam controlled modification of graphene

The defects of atomic scale in graphene layers change the physical and chemical properties of carbon nanostructures. The uncontrolled defects are formed spontaneously already at the stage of preparation of graphene. Defects of a certain type can be created artificially by ion bombardment [118] or by scanning probe lithography [119]. The method of scanning probe lithography makes it possible to modify the structure of graphene with high precision. However, the ion beams scan the graphene faster than the mechanical probe and the diameter of the scanned region can be only a few nanometers. The irradiation by ions is a powerful tool for creating nanostructured surfaces. The potential of ionic beams is very large; they make it possible not only to create vacancies [120–122] and to implant ions [123], but also to tune the electronic structure [118], to change various properties of graphene [124] (including magnetic properties [125, 126]), to purify the surface of graphene [127], and to cut graphene sheets [128].

4.1 Creation of defects in graphene by bombardment

In graphene nanostructures, various defects can be created which affect the electrical, thermal, and mechanical properties of these nanostructures: (1) vacancies and vacancy complexes; (2) three-dimensional defects (humps, hills, dome-like features); (3) implanted atoms of various metals.

(1) Under the action of an ionic beam, mono-, bi-, and polyvacancies, as well as vacancy clusters, can be formed. A single vacancy at the center of graphene influences its electronic properties [120], leading to the formation of a ‘pentagon + dangling bond’ defect, which is energetically favorable. However, because of the thermal motion of carbon atoms around the vacancy, this defect is unstable at temperatures of $T = 1000–1500$ K. Upon bombardment of graphene located on a substrate by Xe atoms with energies of the order of several keV [129], vacancy clusters arise, which prove to be stable at higher temperatures up to 900 K. These vacancies have the shape of a funnel propagating down to the substrate. The vacancies on the substrate, on the contrary, disappear completely at $T = 700$ K. All broken carbon bonds become saturated via the binding to the metallic surface, forming funnel-type vacancy structures.

The influence of defects on the thermal properties of graphene have been studied using the MD model in [122]. Monatomic vacancies and Stone–Wales defects with different

concentrations have been considered. A Stone–Wales defect represents a complex of five- and seven-atom rings that arise from two six-atom rings via the rotation of one of the C–C bonds of the graphene network [130]. In graphene located on a substrate, defects of this kind have sufficiently large lifetime (~ 20 s) and disappear after the process of relaxation [131]. When there is a high concentration of Stone–Wales defects, the scattering centers are distributed over the entire graphene, and its thermal conductivity becomes the same as that of a disordered material. In this case, the diffusion modes dominate the processes of heat transfer, and the temperature dependence of thermal conductivity decreases sharply [122].

(2) In [121], the MD method was used to study the formation on the graphite surface of three-dimensional defects containing several dozen atoms in the form of small hillocks, in which the regular lattice rises above the flat surface by 1–10 Å [121]. The number and the location of such dome-like features remain, as a rule, unaltered [132]. The vacancies are the main factor responsible for the formation of defects. As a result of random strikes of carbon atoms with energies of 0.1–3 keV against the surface of graphite, three types of defects can be formed: surface vacancies, interplanar atoms located under the surface layer, and three-dimensional defects. It has been shown by *ab initio* calculations [121] that no significant change in the valence-electron density caused by an absent atom is observed in the vicinity of vacancies. However, the charge density increases near the atoms surrounding the vacancy. The single atoms located between the planes of graphite can migrate at room temperature [133]. As a result of migration, dimers and clusters are formed between the layers, which serve as sources for the formation of hillocks [134]. According to the results of calculations [121], the dimers and trimers form low and wide hillocks up to 1 Å high. Coarse surface defects are formed as a result of the introduction of an additional adsorbed atom (adatom) into the upper layer of graphite at a sufficiently low energy (≈ 50 eV). This adatom is incorporated into the structure of the surface layer, forming a vertical ring (Fig. 11). Such a structure is stable; the binding energy is -3.3 eV in it. In the region of the upper (rising by 2 Å) atom, a maximum of the valence density of the electron charge is observed in the defect. The probability of the formation of such structures is approximately two orders of magnitude less than that of the formation of vacancies and interlayer clusters. However, these structures prove to be stable for at least 3 ps.

The defects significantly change the electronic states of graphene near the Fermi level, which is an important factor. Many unique properties of graphene are determined by the topology of the bands of its electronic structure in the vicinity

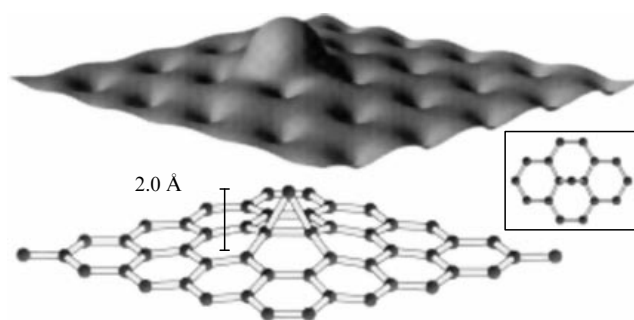


Figure 11. Atomic and electronic structures of a surface three-dimensional defect. In the inset, top view of the defect is shown [121].

of the Dirac point [135–137]. Experimentally obtained graphene flakes deposited onto an SiO_2 substrate were bombarded by 30-eV Ar^+ ions [118]. As a result, defects formed in the form of hillocks several angstroms high. In the vicinity of defects, large fluctuations of electron density are clearly observed, whose origin is due to the interference of electrons scattered at defects. Similar density oscillations were observed in graphite [138], carbon tubes [139], and two-layer graphene [140]. The defects can also significantly affect the Fermi velocity, mainly decreasing it. The possibility of tuning the electronic structure of graphene via the creation of defects opens a promising field in the application of graphene-based electronics.

(3) The mechanism of graphene doping by single atoms of metals includes two consecutive stages: the creation of vacancies by a high-energy beam of ions or atoms; and the filling of these vacancies by atoms of metals. The binding energy in the metal–vacancy complex proves to be sufficient to provide its stability. The structure of the formed vacancy depends strongly on the energy [141] and dimension [142] of the incident particles. Monovacancies and divacancies are created with a greater probability under the effect of beams with energies of the order of 100 eV [143]. Upon irradiation of graphene, mono-, di-, and trivacancies were obtained both experimentally and by MD simulation [144]. The type of vacancy depends on the site which the bombarding atom hits into. If the atom hits into the C–C bond, mainly divacancies are formed; the ‘atom–atom’ collision leads to the formation of a monovacancy; if the bombarding atom hits the center of a hexagonal ring, multivacancies are mainly formed due to the removal of five or six C atoms. Then, Pt atoms are deposited into the formed vacancies (Figs 12a, 12b). The calculations show that the barrier for the migration of Pt atoms is 0.2–0.8 eV. This is sufficient for obtaining a stable metal–vacancy structure even at room temperature. Calculations based on the DFT method yield lower energies of the Pt–vacancy complexes (~ 6 eV), which explains their stability under prolonged electron irradiation (Fig. 12c).

The MD method was used to study graphene bombarded by normally incident neutral carbon atoms at various energies and $T = 300$ K [145]. At energies below 1 eV, the dominating process is reflection, which is mainly caused by the repulsive interaction between the incident atoms and π electrons of the

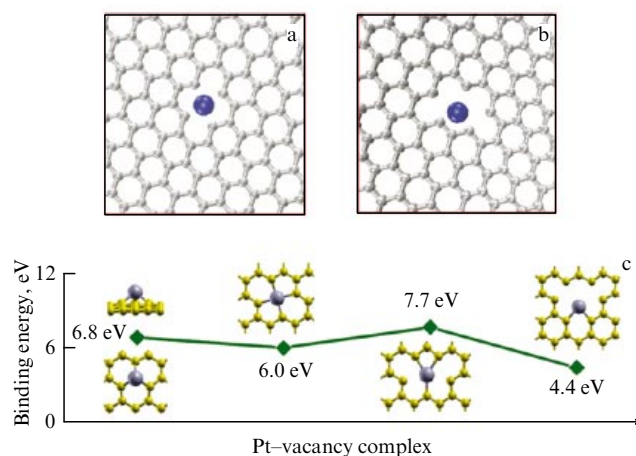


Figure 12. Diagram implantation of a Pt atom into (a) a divacancy and (b) a trivacancy. (c) Binding energy for various configurations of the Pt–vacancy complex [144].

graphene sheet. The energy of the incident beam exceeding 1 eV proves to be sufficient to overcome this repulsion, and the process of absorption becomes predominant at energies of up to 100 eV. In the same energy range, defects such as adatoms, monovacancies, and divacancies begin to arise, which are reconstructed with time. In the end of the calculation, six-atom and eight-atom rings are formed.

4.2 Cutting of graphene by ion beams

One method of cutting graphene is based on the use of a focused beam [146, 147] of helium ions with an energy of 30 keV. Such a beam stably sputters carbon atoms from the preliminarily chosen region of graphene. In this case, different mechanisms of energy transfer from the incident ion beam to the carbon structure are realized [148]. The process of cutting graphene by an incident ion beam is based on the formation of mono- and divacancies or vacancy complexes.

The MD method was used to study processes of the formation of defects in graphene upon its irradiation by ions of various chemical elements (Ar, Xe, Kr, He, Ne). The angles of incidence were varied from 0 to 88°; the energies used were varied from several dozen electron-volts to 10 MeV [128]. At low energies (below 1 keV) and with a normally incident beam (zero angle of incidence), the most probable defect to be formed is a monovacancy. For obtaining the predominant formation of divacancies, relatively small angles of incidence (less than 38°) and low energies of ions (less than 5 keV) are required. However, with increasing energy (up to 20 keV) at the same small angles of incidence, vacancy complexes begin forming. Upon a further increase in the angle of incidence (up to 80°) and the energy of the ionic beam (up to 40 keV), the dominating defect again becomes monovacancy. This factor proved to be determining for the process of cutting graphene at a fixed energy. No defects are formed at very large angles of incidence ($\approx 80^\circ$) and low energies of the incident beam (less than 1 keV). In the case of a glancing angle ($\approx 88^\circ$), the ions interact only with the far rows of atoms, and if the energies are low, then the ions are reflected from the sheet without knocking atoms from the graphene. However, when the energy increases (up to 40 keV), the ions of the glancing beam penetrate through the graphene sheet and create vacancy complexes with a large probability. At low energies (< 1 keV), when the beam energy only suffices to displace some carbon atoms, the amorphization of graphene takes place. The amorphized atoms do not lose their bonding with the sheet, remaining in the form of adatoms on the surface.

Experiments in [146] confirmed that a focused beam of He ions can be used for cutting graphene with very high precision. If the incident beam is directed normal to the sheet surface, part of the collisions lead to a sputtering of carbon atoms, and part to amorphization, which is undesirable for the process of precise cutting. The quality of cut edges can be improved by using an ion beam with an angle of incidence of $\approx 60^\circ$. The bombardment of the target at an angle leads to a decrease in the probability of the formation of collision cascades in the plane and of local amorphization. The obliquely incident He ions at sufficiently high energies (30 keV) create single vacancies, which makes it possible to obtain pure edges upon the cutting of graphene by an ion beam.

It was established in computer experiments [128] that for the normal incidence of a helium beam the fraction of scattered C atoms is $\sim 6\%$; the other part is amorphized. However, when the angle of incidence of the ion beam is 62.5°

at the energy of 30 keV, the number of scattered carbon atoms increases by a factor of three, i.e., the cutting beam acts more efficiently.

4.3 Magnetism determined by vacancy complexes in graphene

The perfect graphene does not have a magnetic moment in the absence of an external magnetic field and, consequently, does not have ferromagnetic properties. Various defects and the topological structure (long-range ordering of paired spins) can serve as sources of ferromagnetism in graphene. The experimental hysteresis loops obtained upon magnetization [149] show that graphene sheets prepared at various temperatures exhibit a weak ferromagnetic effect at room temperature. The magnetism in a graphene sheet is created by a certain organization of defects (vacancies) [150]. One of the important properties of graphene is edge magnetism, which is due to the localization of electronic states on zigzag edges. It has been shown theoretically in [151] that graphene with zigzag edges and a ferromagnetic order is stable at room temperature (with an energy of 0.3–0.5 eV at the Fermi level). This magnetism can be controlled by an external electrical field [152] or, for example, by using graphene islands on an SiC substrate [126]. In the process of growth of graphene islands, energetically favorable structures incorporated into the substrate, which have no dangling bonds, are formed. The islands with zigzag edges have states localized at the edges, which can lead to magnetoelectric effects.

The carriers of magnetism are in this case orbital interactions or spins of electrons. States with ‘spin up’ and ‘spin down’ for the monovacancy in graphene are asymmetric near the Fermi level. This leads to a splitting and polarization of spin in the vacancy band [153]. The closely located vacancies behave independently if the spacing between them is more than 7 Å [154]. The magnetic moment depends nonmonotonically on the spacing between the vacancies. At the smallest spacing, it is equal to $1.15\mu_B$; at the maximum spacing (i.e., at $r \sim 7$ Å), 1.45 – $1.53\mu_B$ [155].

In the MD experiment, the polarization of the spin for mono-, tri-, and tetravacancies was calculated; it was found that the magnetic moment is localized near the vacancy cluster [156]. In large vacancy complexes, the magnetic moment is concentrated at the edges of the defect. It gradually becomes diffuse with movement from the defect and increases as the size of the vacancy increases [157]. The energy band in graphene with a vacancy is absent.

Various configurations of the ‘graphene + vacancy cluster’ system have been studied by *ab initio* simulation in [125]. The symmetrical spin-up and spin-down states have been obtained by creating a divacancy in graphene, i.e., in the absence of polarization and, consequently, at a zero magnetic moment. For vacancy clusters containing from 3 to 6 defects, a nonzero magnetic moment localized near the vacancy was observed. Figure 13 displays various configurations of the graphene + vacancy cluster system depending on the number of carbon atoms removed from the graphene sheet. According to MD calculations [125], the magnetic moment of the configuration V4_3 is equal to zero, since the function of the density of spin-up and spin-down states is symmetrical. The V6_2 configuration is more favorable energetically than V6_1 (the magnetic moments are $4.50\mu_B$ and $5.49\mu_B$, respectively [153]).

The influence of various metallic atoms implanted into vacancies was studied in terms of the DFT [144]. According to these data, Pt–vacancy complexes are nonmagnetic at

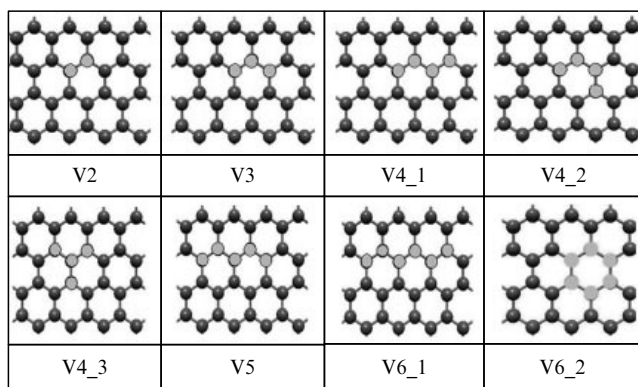


Figure 13. Various configurations of the graphene + vacancy-cluster system [125].

various numbers of vacancies (1 to 4); Co–vacancy complexes, on the contrary, have a magnetic moment. The local density of states at the Fermi level corresponds, mainly, to localized states around the Co atom. The total spin moment of the Co–monovacancy system is equal to $1.0 \mu_B$; the contribution from the Co atom in this case is $0.44 \mu_B$. However, in the Co–divacancy system, the total moment of the spin equal to $1.56 \mu_B$ contains a contribution equal to $1.50 \mu_B$ from Co atoms (mainly due to 3d orbitals); the other part comes from the 2d orbitals of carbon.

5. Physicochemical properties of graphene edges

5.1 Reactive ability of zigzag edges of graphene

At the boundary determined by the edge of graphene, a complete delocalization of π electrons occurs. The electronic structure of a nanoribbon depends on the geometry of the edges [158, 159]. The localized state established at the zigzag edge leads to interesting chemical properties.

Calculations based on the DFT with the use of the generalized gradient approximation (GGA) for exchange correlations of electrons made it possible to study the magnetic, electronic, and chemical properties of graphene nanoribbons with zigzag edges saturated with hydrogen [160]. Owing to the unbound character of the localized state and the proximity of the flat branch of the electronic spectrum to the Fermi level, the zigzag edges can play the role of radicals. In graphene ribbon with zigzag edges, the unpaired π electrons distributed over the zigzag edges bring an average charge of $-0.14e$ to each atom belonging to the edge. Thus, the edges of the ribbon acquire a ‘radical-like’ character, i.e., acquire reactive ability.

The calculation of the bond-dissociation energy (BDE) has shown that the strength of the C–H bond formed at the zigzag edge reaches only 60% of the strength of the analogous molecular bond between the carbon radical and hydrogen. The calculation of the BDE between carbon atoms belonging to the edge and common radicals have shown that the BDE of C– X (where $X = \text{OH}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}, \text{or I}$) systems is equal to 40–80% of the experimental $\text{C}(\text{sp}^3) - X$ energy. In addition, the zigzag edges of a zigzag nanoribbon of graphene (ZNRG) have a greater BDE than that of nanotubes and nanoribbons with armchair-type edges.

The low electron density at the edge of the ribbon is because of the collective character of the interaction of the C

atom belonging to the edge with other (not ‘outer’) atoms of graphene and also because of the interaction between the radicals. The ground state of a nanoribbon with zigzag edges is antiferromagnetic (AFM); its energy is only insignificantly lower than that of the ferromagnetic state. In the AFM phase, the C atoms at the edges have a magnetic moment of $\sim 0.14 \mu_B$ and the local density of states is characterized by a sharp peak below the Fermi level for one of the spins and above it for the other spin.

5.2 Adsorption of transition metals by a zigzag nanoribbon

The electronic properties of a nanoribbon can be changed by adsorption or doping with foreign atoms or molecules [161, 162]. The electronic and transport properties of graphene nanoribbons doped with nickel have been studied in [163], and the structure of graphene sheets with trapped nickel in [164].

The structure and electronic properties of ZNRG with adsorbed atoms of transition metals (Co and Ni) have been studied by the DFT method in [165], where the exchange correlation potential was represented in the generalized-gradient approximation [166]. A rectangular piece of a ZNRG was considered, containing 48 carbon atoms and one or two adsorbed atoms. The edges were decorated with hydrogen atoms; this led to the neutralization of the valency of carbon atoms. Five configurations with adsorbed atoms of transition metals have been investigated: configuration (a) with one Ni atom adsorbed at the edge; configuration (b) with two adsorbed Ni atoms, one at each edge of the graphene ribbon; configurations (c) and (d) that are analogous to configurations (a) and (b), respectively, in which an Ni atom is replaced by a Co atom; and a configuration (e), in which an Ni atom is adsorbed at one edge, and a Co atom at the other edge. In each case, upon adsorption of a transition-metal atom, six Ni(Co)–C bonds were formed. Table 3 contains the bond lengths for these five configurations after complete relaxation. In the case of configurations (b), (d), and (e), data are given for each of the adatoms Ni or Co. The shortest bond corresponds to the strongest interactions between the adatoms of the transition metal and carbon atom. In the case of adsorption of two metal atoms, all lengths of the metal–carbon bonds change because of the interaction between metal atoms. The short bonds for Co are smaller than in the case of Ni because of the greater atomic radius of the Ni atom. In configuration (e), the length of the Ni–C bond is greater than the length of the Co–C bond for the same reason. The interaction between two Co atoms is weaker than that between two Ni atoms. The changes in the structure caused by relaxation affect the electronic properties of the configurations. The appearance of each metal atom leads to

Table 3. Lengths of Co–C and Ni–C bonds for different atoms adsorbed on zigzag graphene ribbon [165].

Configuration	Bond length (Ni–C or Co–C), Å					
(a), Ni atom	2.065	1.992	2.071	2.091	2.078	2.085
(b), 1st Ni atom	2.080	1.987	2.081	2.067	2.081	2.066
(b), 2nd Ni atom	2.105	1.997	2.107	2.065	2.058	2.063
(c), Co atom	2.071	1.937	2.083	2.045	2.046	2.032
(d), 1st Co atom	2.089	1.949	2.098	2.028	2.024	2.023
(d), 2nd Co atom	2.085	1.946	2.076	2.025	2.032	2.030
(e), Ni atom	2.077	1.943	2.081	2.028	2.028	2.026
(e), Co atom	2.083	1.989	2.087	2.069	2.081	2.065

Table 4. Charge transferred from adatom to the zigzag graphene ribbon in the case of different configurations* [165].

Configuration	Charge/ e	
	Atom 1	Atom 2
(a)	0.239	0.224
(b)	0.222	
(c)	0.196	
(d)	0.18	0.175
(e)	0.179	0.221

* e is the elementary electrical charge.

Table 5. Energy-band gap for two spins for configurations in the absence of metal and for different configurations in the presence of adsorbed metal atoms [165].

Configuration	α -spin, eV	β -spin, eV
Without Ni and Co	0.56	0.56
(a)	0.31	0.44
(b)	0.39	0.39
(c)	0.26	0.44
(d)	0.26	0.26
(e)	0.29	0.37

the appearance of an additional subbranch in the electronic spectrum, which is related to the hybridization between the impurity states (Ni or Co) and π orbitals of the nanoribbon. In configuration (e), two new subbranches also appear in the conduction branch. The Fermi level of configurations (a)–(e) shifts up compared to the analogous characteristic of the ZNRG free of metal. This shift can be explained by a change in the effective Coulomb potential because of the charge transfer.

The calculated portions of the transferred charges are presented in Table 4. An increase in the number of metal atoms in the ZNRG leads to a decrease in the magnitude of the charge transferred from the metal atom to the ribbon. The charge transferred from the Co atom is always less than that transferred from an Ni atom. This is related to a stronger interaction between the Ni atom and the graphene ribbon. The energy-band gap (EBG) that was determined in [165] for two (α and β) spins is given in Table 5. The largest EBG corresponds to a nanoribbon without metal atoms. The addition of a second metal atom leads to the leveling of the EBG for the α and β spins. In the case of adsorption of Ni, the EBG is greater than upon capture of a Co atom by the graphene ribbon. A comparison with configurations (b) and (d) shows that the EBG of the two spins in configuration (e) reflects the hybrid interaction between the Ni(Co) atoms and the nanoribbon. Thus, the ZNRG with an adsorbed Co atom is closer in its electronic properties to semimetals than the graphene ribbon with a deposited Ni atom.

5.3 Changes in the transport properties, passivation, and reconstruction of graphene edges

Let us now consider the effect of other atoms and atomic groups on the electronic properties of the ZNRG. In [167], the structures of the branches of the electronic spectra of ZNRG have been calculated in terms of the local DFT. The neutralization of the dangling bonds by hydrogen, oxygen, and hydroxyl and imine (nitrous analog of aldehydes) groups has been considered. The compensation of sp^2 - σ orbitals by hydrogen atoms and by hydroxyl groups led to the appear-

ance of two separated stable spin-polarized states. In this case, σ branches are formed in the electronic spectrum that lie far from the Fermi level. On the contrary, the oxygen atoms and imine groups yield spin-unpolarized equilibrium states with a complex structure of the branches in the electronic spectrum. In this case, one of the σ branches intersected the Fermi level, and the excessive electron per unit cell prevented the formation of a spin-polarized state. Here, just as the case where the atoms of hydrogen and the hydroxyl groups are fixed at the edges, a transfer of a charge to the ribbon occurs, since oxygen and the imine group are more electronegative than carbon. The obtained structure of the branches of the spectrum indicates a strong change in the electron transport properties.

In the absence of a control over the state of the edges of the ZNRG, a problem arises of the reproduction of the desired transport properties. On the other hand, the possibility of controlling these properties makes it possible to govern them for various applications. For example, the attachment of hydrogen atoms and hydroxyl groups to the edges of the ZNRG makes it possible to carry out some control in spintronics devices [168], and the addition of oxygen or an imine group to the edges makes it possible to use the ribbon as a metallic or quasi-metallic connection.

It is known that strong correlations lead to new phenomena, which can appear because of the modification of the quasi-one-dimensional edges of graphene [169]. In [170], an original reconstruction of the most important edges of graphene was suggested. As a result of a rearrangement of a zigzag edge in which two hexagons are replaced by a pentagon and a heptagon, a $zz(57)$ -type edge was obtained, as shown in Fig. 14a. The reconstruction of an armchair-type edge, in

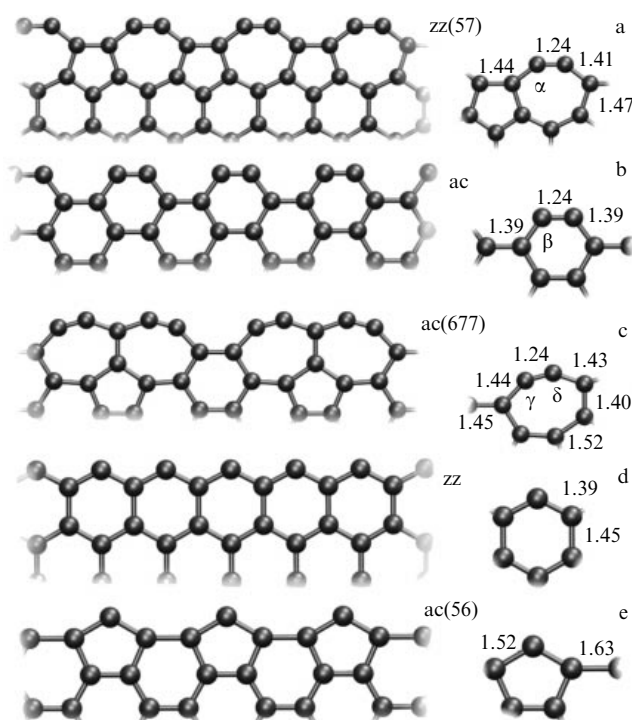


Figure 14. Geometry of graphene edges: (a) reconstructed zigzag edge $zz(57)$; (b) armchair-type edge ac ; (c) reconstructed armchair edge $ac(677)$; (d) zigzag edge zz ; (e) edge of a pentagonal armchair type $ac(56)$. The numbers in parentheses indicate the number of vertices in the polygons composing the edge. All geometrical figures are located strictly in the plane [170].

which two separated hexagons (armrests) are transformed into contacting heptagons via the Stone–Wales mechanism, gives an ac(677)-type edge shown in Fig. 14c. The pentagonal reconstruction of the armchair-type edge ac(56) differs from ac(677) only a little, since it is based on the removal of carbon atoms from ‘far’ armrests (Fig. 14e). The unreconstructed edges of the armchair and zigzag types are shown in Figs 14b and 14d, respectively.

The total energy E of a graphene nanoribbon is written as follows:

$$E = -NE_{\text{gr}} + LE_{\text{edge}}, \quad (9)$$

where N is the number of carbon atoms; L is the total length of edges; E_{gr} is the cohesion energy of graphene; and E_{edge} is the energy of the edges. The energy of an armchair-type edge calculated in terms of the DFT is lower than that of the zigzag edge, just as in the case of nanotubes [171]. However, the reconstruction of a zigzag edge gives a lower energy and, consequently, an edge that is more favorable for graphene than any of the reconstructions of the armchair-type edges. The energy of the ac(677) edge only insignificantly exceeds the energy of the armchair-type edge, whereas the ac(56) edge has the greatest energy. The ac(56) edge is subject to the effect of dangling bonds, just as in the case of the zigzag edge. Nevertheless, the ac(56) edges can appear during the growth of graphene [171].

It is of interest to study the effect of hydrogen adsorbed on the reconstructed edges. The weaker adsorption in the case of armchair edges (4.36 eV) as compared to that for zigzag edges (5.36 eV) is due to the presence of triple bonds in the armchair edges. In a similar way, the lower adsorption for the zz(57) (3.82 eV) and ac(677) (3.64 eV) indicates the weakness of the unsaturated bonds. The adsorption at the ac(56) edge (5.58 eV) is stronger. More complete data on the energy properties of the edges are given in Table 6. The ‘best’ edges for hydrogen adsorption are the common armchair-type and zigzag-type edges because of the existence of unsaturated bonds in them. On the contrary, the weak unsaturated bonds and low energy of adsorption cause high values of the energy $E_{\text{edge+ads}}$ for the zz(57) and ac(677) edges. The ac(56) edge, in spite of the high energy of adsorption for it, is not favorable for hydrogen adsorption either, since it has a large energy of deformation.

The reconstructions of edges discussed in [170] are expected at the terraces of graphene in view of the weak interaction (5.6 meV per atom) between the basal planes [172]. The images obtained using scanning tunneling microscope frequently demonstrate nonregular and diffuse edges (mainly passivated armchair-type edges), probably because of

the reconstruction rather than the insufficient atomic resolution [173]. The zz(57) edge creates a branch in the electronic spectrum that is near the Fermi level. Thereby, this edge, unlike the convenient edges of graphene, causes enhanced conductivity. The stable chemical reconstruction plays an important role in the formation of angular junctions in nanotubes [174] and in the closing of nanotubes after cutting [175], as well as in other systems obtained by joining graphene sheets.

6. Effect of temperature on the strength of graphene

6.1 Determination of the melting temperature of graphene

In many applications, graphene is used in the form of ribbons. In [176], the melting of a graphene ribbon in the form of a rectangle $2 \text{ nm} \times 3.5 \text{ nm}$ in size was studied. The C atoms that form the perimeter of the rectangle were assumed to be immobile during the entire calculation. Thus, the weakest sites of graphene were artificially protected from thermal fluctuations. The investigation was performed with a step in temperature equal to 100 K. At $T = 3400 \text{ K}$, the C atoms nearest the immobile atoms left their sites and, along with the fixed atoms, formed the boundary of the graphene ribbon. Therefore, in one of the corners of the rectangle, a cavity was formed, and the hexagonal shape of separate hexagons was distorted at its boundaries. The temperature in the model was maintained via a Nosé–Hoover thermostat [177, 178]. The application of this algorithm led to strong continuous fluctuations of the temperature around its average value of 3400 K.

Taking into account the entire set of the above changes in the model, the authors of [174] interpreted the temperature equal to 3400 K as the melting temperature T_{m} of the nanoribbon. This is the lowest estimate of T_{m} for graphene. This value is even lower than that for graphite ($\approx 4000 \text{ K}$) [179]. Most probably, the changes observed in [179] refer to the melting of graphene boundaries (and by no means to all of them), whereas no liquid phase was observed outside the region of the boundaries in fact. Thus, the effect observed at 3400 K is, in fact, the thermal instability of graphene edges rather than melting.

In [180], the melting temperature of graphene was determined by the Monte Carlo (MC) method in the process of the simulation of melting of a graphite system consisting of 16,128 atoms (systems of a smaller size were also considered) under periodic boundary conditions. According to the estimation of the authors of [180], the upper limit for the temperature T_{m} for graphene should be equal to 4900 K, which is higher than that for fullerenes (4000 K) [181] and nanotubes (4800 K) [182].

The MC simulation of the melting process of graphite [183] with a long-range carbon bond-order potential (LCBOP-II) [184] has shown that at $T = 3000 \text{ K}$ a layer-by-layer splitting of graphite with the formation of graphene layers starts. The melting of graphene that was studied in [180] can be considered as the following step in the thermal decomposition of graphite. In this case, the two-dimensional (2D) graphene layers were melted into a three-dimensional (3D) liquid network and one-dimensional (1D) chains. The short-range order in graphene was destroyed because of the formation of pentagon–heptagon pairs, which in this system represent dislocations (Stone–Wales defects) arising as a result of the rotation of carbon bonds.

Table 6. Energy characteristics* of graphene edges upon hydrogen adsorption [171].

Edge	zz(57)	Armchair ac	ac(677)	Zigzag zz	ac(56)
Energy					
$E_{\text{edge}}, \text{eV } \text{\AA}^{-1}$	0.96	0.98	1.11	1.31	1.51
$E_{\text{edge}}^*, \text{eV per atom}$	2.36	2.09	2.30	3.22	6.43
$E_{\text{ads}}, \text{eV}$	3.82	4.36	3.64	5.36	5.58
$E_{\text{edge+ads}}, \text{eV } \text{\AA}^{-1}$	0.34	0.01	0.45	0.06	0.74

* E_{edge}^* is the energy of an edge (in eV per atom), E_{ads} is the energy of hydrogen adsorption, $E_{\text{edge+ads}}$ is the energy of an edge in the presence of hydrogen.

The Stone–Wales defects create regions of local symmetry of fifth and seventh order in a two-dimensional crystal, i.e., symmetry that is incompatible with an infinite regular packing of atoms. According to the authors of [180], it is precisely these defects that initiate melting in graphene. Then, octagons are formed, which can serve as precursors of spontaneous melting. Upon melting, an entangled 3D network is formed, consisting of chains that tightly connect the three-coordinated atoms. This structure, which has a low density, is a polymeric gel rather than a simple liquid. The simulation indeed made it possible to observe a state in which both solid and liquid phases exist simultaneously. However, the periodic boundary conditions eliminate the boundaries of the 2D crystal, i.e., precisely those regions in which melting should start. The simulation of melting of various three-dimensional systems in this case leads to overestimated values of T_m [185]. Note that T_m of small graphene flakes is lower than T_m of extended graphene sheets or nanoribbons. Defects existing in the graphene flakes decrease T_m ; the hydrogen passivation of the flakes, on the contrary, increases it.

6.2 Mechanical and energy properties of nanocomposites

The high ability to stretch and the high rigidity of single-layer graphene can be used for strengthening of composite materials [186–188]. At present, of significant interest is the application of metals as matrix materials for nanocomposites [189–191]. The mechanical properties of composites depend substantially on the material and strength of interphase interfaces. The perfect sp^2 -hybridized structure of graphene possesses only a limited ability to form strong bonds of any type with the surrounding metallic matrix.

Investigations have shown that Au, Al, Fe, Pb, and Zn exhibit poor wetting of the surface of carbon nanotubes [192]. Graphene, just like nanotubes, demonstrates bad wetting at the interphase surface with metallic matrices. However, some metals, e.g., Ni, Pt, Pd, and Ti, become bound quite strongly with pure carbon tubes [193, 194]. Therefore, a possibility appears to improve the adhesion between the chosen metallic matrix and graphene. By coating graphene with an appropriate metal, a metal/graphene composite can be obtained whose mechanical properties depend on the adhesion properties of the metallic matrix and metallic coating. The nickel substrate changes the band structure of graphene, imparting to it a partly semiconducting behavior, whereas, for instance, a copper substrate exerts a minimum effect on the band structure of graphene [195].

In [192], the method of classical molecular dynamics was used to study effects that appear when coating a single-layer graphene sheet with nickel with its subsequent incorporation into the aluminum matrix and uniaxial extension of the obtained composite. The C–C interaction was described by the second-generation Brenner potential [196]. All other interactions were simulated by many-particle potentials taken from [197]. The graphene was coated uniformly by a monolayer of nickel on both sides in such a manner that the Ni atoms were located against the centers of the hexagonal cells. The Ni-coated and Ni-uncoated graphene sheets were inserted into the aluminum matrix in parallel to the atomic layers of the plane (100). The tension of the composite was performed along the direction (001) of the aluminum matrix. It was shown that the Young's modulus of the graphene/nickel-coated-aluminum composite is greater than that of the analogous composite without nickel, although the modulus Y and the ultimate strength of the graphene sheet decrease when

the sheet is coated with nickel. Thus, the coating of graphene with nickel can be used to strengthen the graphene/aluminum composite.

6.3 Thermal stability of graphene and its nickel and aluminum coatings

In [198–200], we used the MD method to study the stability of single-layer and two-layer graphene together with metal films, coating it from two sides upon heating to 3000 K. The interatomic bonds in graphene were simulated using the Tersoff potential [201, 202]. To prevent the resulting torque, the torsional component of the force created by the atoms of neighboring nodes was eliminated in each node of the graphene sheet [203]. The M – M interaction (where $M = \text{Al, Ni}$) was specified by the Sutton–Chen potential [204]; the M – C interaction was specified by the Morse potential [205, 206].

Figure 15 displays configurations of the nickel–two-layer-graphene system with a one-side coating of the graphene with a metal that refer to the time moment of 200 ps and temperatures of 300 and 3300 K [200]. With increasing temperature, the graphene sheets become deformed, being compressed in the middle part in the armchair-type direction. At 3300 K, this leads to the bulging of the corners of the sheets. In the vicinity of the armchair-type edges of the sheets, some atomic disordering is observed, but not a single C atom broke from its sheet at $T = 3300$ K. More than half of the Ni atoms become evaporated at 3300 K.

The spectra of the components $V_{xy}(\omega)$ and $V_z(\omega)$ of the Fourier transform of the average autocorrelation function $V(\omega)$ of the atomic velocities for the individual vibrations of the atoms of the Ni film located on a single-layer graphene sheet at 3300 K have a similar shape both for horizontal and vertical vibrations (Fig. 16a) [200]. In these spectra (both $V_{xy}(\omega)$ and $V_z(\omega)$) there are, apart from the main peak at the frequency of $1.8 \times 10^{12} \text{ s}^{-1}$, several additional peaks of smaller intensity, which are initiated by the vibrations of carbon atoms. In the frequency spectra (of both $V_{xy}(\omega)$ and $V_z(\omega)$) of the Ni film on two-layer graphene, the main peak is localized at the frequency of $2.3 \times 10^{12} \text{ s}^{-1}$ (Fig. 16b). As in the case shown in Fig. 16a, the principal vibrations in the horizontal direction are pronounced more strongly than those in the vertical direction. The $V_z(\omega)$ spectrum of the film on the two-layer graphene at lower frequencies has a considerably greater intensity, which is caused by the effect of the graphene-lattice dynamics.

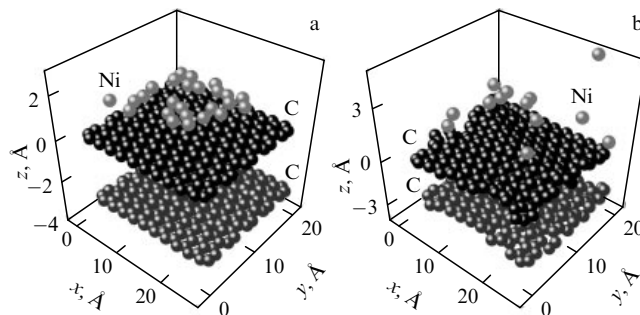


Figure 15. Structure of a two-layer graphene with a nickel film, corresponding to the time moment 200 ps, at temperatures (a) 300 and (b) 3300 K [200].

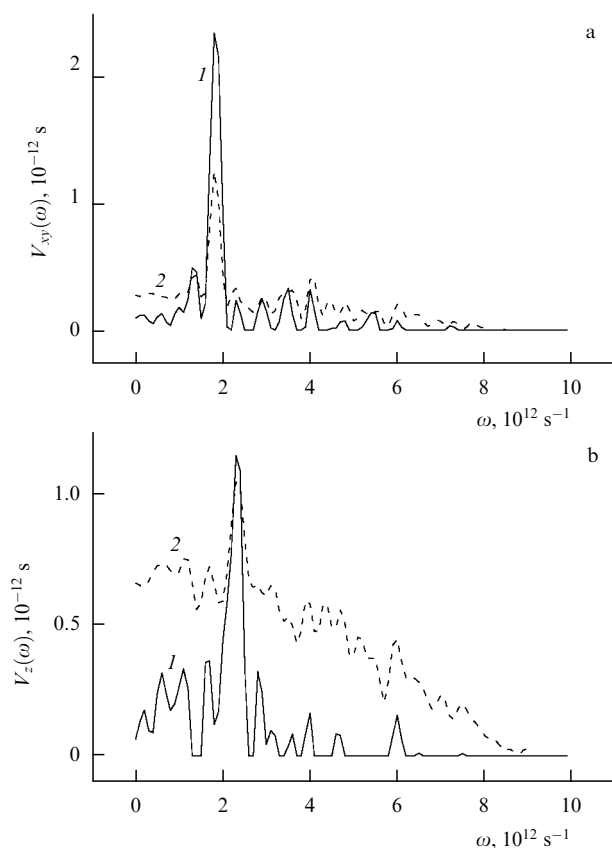


Figure 16. Spectra of individual ((1) horizontal and (2) vertical) vibrations of Ni atoms for an Ni film on (a) single-layer and (b) two-layer graphene [200]. $V(\omega)$ is the Fourier transform of the average autocorrelation function of the velocities of atoms.

A significant difference in the high-temperature behavior of Ni atoms on the two-layer graphene from their behavior on the single-layer graphene is their higher vertical mobility, which increases in a wavy manner with increasing temperature. Correspondingly, the spectrum of the individual vibrations of Ni atoms on the two-layer graphene has a considerably greater intensity at lower frequencies.

The high values of the stress components σ_{xx} and σ_{yy} at $T = 300$ K decrease, as a rule, at a temperature of 1300 K both when the film is on the single-layer or on the two-layer graphene (Fig. 17a) [200]. Generally, the σ_{xx} and σ_{yy} components behave, except for some features in the temperature range of 1300–2800 K, identically in both cases. The values of the σ_{xx} and σ_{yy} components are mainly determined by the structure of the very film and only weakly depend on the state of the substrate. The σ_{zz} component behaves differently with increasing temperature (Fig. 17b). In both cases (when the film is located either on the single-layer or on two-layer graphene), σ_{zz} is initially characterized by very low values, but with increasing temperature it tends to an increase.

The stability of aluminum films on graphene depends on their number. Upon single-sided coating of the graphene sheet with aluminum, Al atoms are preserved on the surface of graphene even at the temperature of 3300 K, whereas the two-sided coating leads to the evaporation of all Al atoms at a temperature of 1800 K. Initially (at $T < 1300$ K), the Al atoms are collected into a dense flat droplet, decreasing the size of the film predominantly in the armchair direction. The

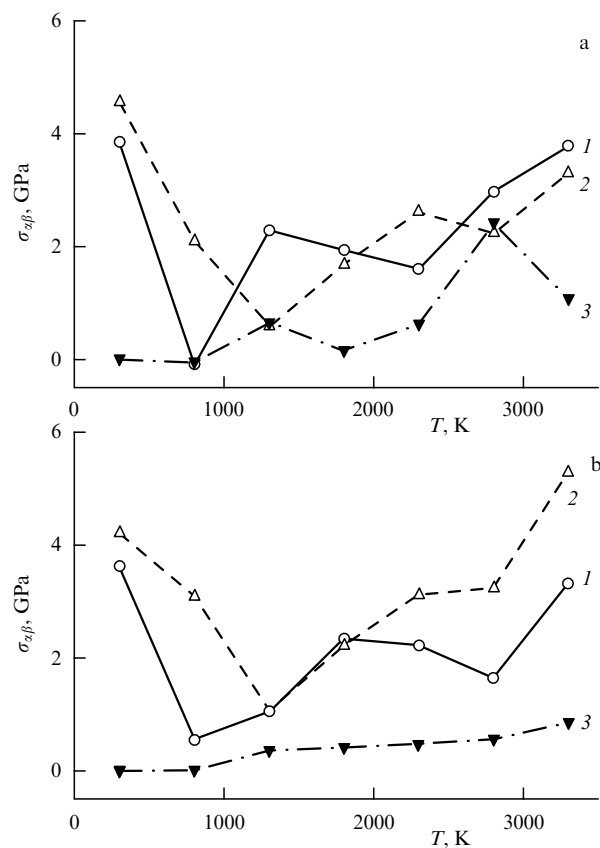


Figure 17. Components of the stress tensor σ_{xx} (line 1), σ_{yy} (line 2), and σ_{zz} (line 3) for a nickel film on (a) single-layer and (b) two-layer graphene [200].

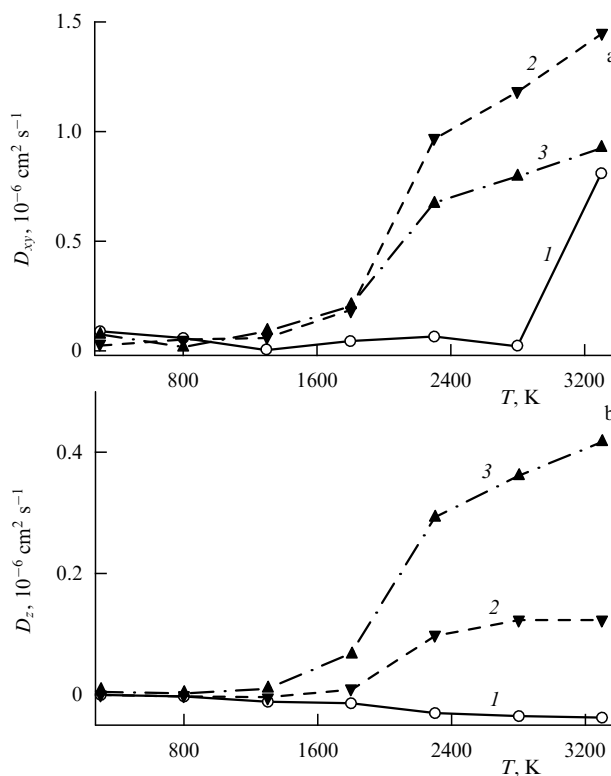


Figure 18. (a) Horizontal (D_{xy}) and (b) vertical (D_z) components of the self-diffusion coefficient in Al films: (1) a single film of Al on a graphene sheet; (2) upper and (3) lower Al films on a graphene sheet with a two-sided coating [198].

coefficients of self-diffusion of Al atoms along both horizontal and vertical directions increase substantially at $T > 1800$ K in the case of the two-sided coating of graphene by aluminum and retain low values with increasing temperature up to 2800 K in the case of the single-sided coating (Fig. 18) [198].

For the calculation of stresses that appear in graphene, the graphene sheet was divided into elementary regions. The atomic stresses $\sigma_J^i(n)$ per elementary n th region for each of the directions x , y , and z with a current index J are determined via the calculation of the kinetic energies of atoms in this region and of the projections of forces f_J^i acting on the n th region from the side of all other atoms:

$$\sigma_J^i(n) = \frac{1}{k} \left\langle \sum_i^k \frac{1}{\Omega} (mv_J^i v_J^i) \right\rangle + \frac{1}{S_n} \left\langle \sum_i^k (f_J^i) \right\rangle, \quad (10)$$

where k is the number of atoms in the n th region; Ω is the volume per atom; m is the mass of an atom; v_J^i is the J -projection of the velocity of the i th atom; S_n is the area of the n th region; and $\langle \dots \rangle$ means averaging over time. The compressive stresses with such a definition can be positive or negative (can have a plus or minus sign) in accordance with the directions of the forces f_J^i . It is this feature that distinguishes the microscopic stresses $\sigma_J^i(n)$ from the macroscopic stress $\bar{\sigma}_J < 0$.

In the presence of one metallic film on the graphene sheet, the amplitudes of the σ_{zx} stresses (Fig. 19a) change in a considerably smaller range than those of the σ_{zy} stresses (Fig. 19b) [198]. Consequently, the arising interatomic forces acting in the armchair directions exceed the forces oriented in

the zigzag directions. The temperature behavior of the stress σ_{zz} acting in the graphene sheet, which is caused by vertical forces, is somewhat different than that of the σ_{zx} and σ_{zy} stresses, which are determined by horizontal forces (Fig. 19c). The maximum absolute values of the σ_{zz} stress at $T = 300$ K are realized at small values of x at the edge rather than in the middle zone of the sheet. At 1300 K, in the middle region of the sheet a high peak of the stress σ_{zz} appears; the lower peaks of σ_{zz} stress are located closer to the edges of the sheet. The high peak is caused by the vertical displacements of closely grouped Al atoms. These displacements also lead to a sharp decrease in the stress σ_{zx} in the metallic film. The σ_{zz} stresses in the graphene sheet become ‘resolved’ upon a further increase in temperature, but even at $T = 3300$ K the amplitude of fluctuations of σ_{zz} noticeably exceeds those for σ_{zx} and σ_{zy} at this temperature.

Simulations have shown that the monatomic film of aluminum on a two-layer graphene has a high thermal stability, which is due to the high temperature stability of the graphene structure and to its high adsorption properties. The Al atoms move freely on the surface of the substrate, forming a monolayer island with a close packing of atoms. A stronger decrease in the size of the metallic film is observed in the transverse direction, which in graphene is determined as the armchair direction. No pronounced correlation between the kinetic properties of the aluminum film and corresponding properties of the graphene sheets is observed. The horizontal mobility of C atoms at $T = 3300$ K increases sharply, which agrees with the behavior of the $D_{xy}(T)$ function for aluminum, but the vertical mobility of C atoms behaves rather ambiguously (Fig. 20) [198].

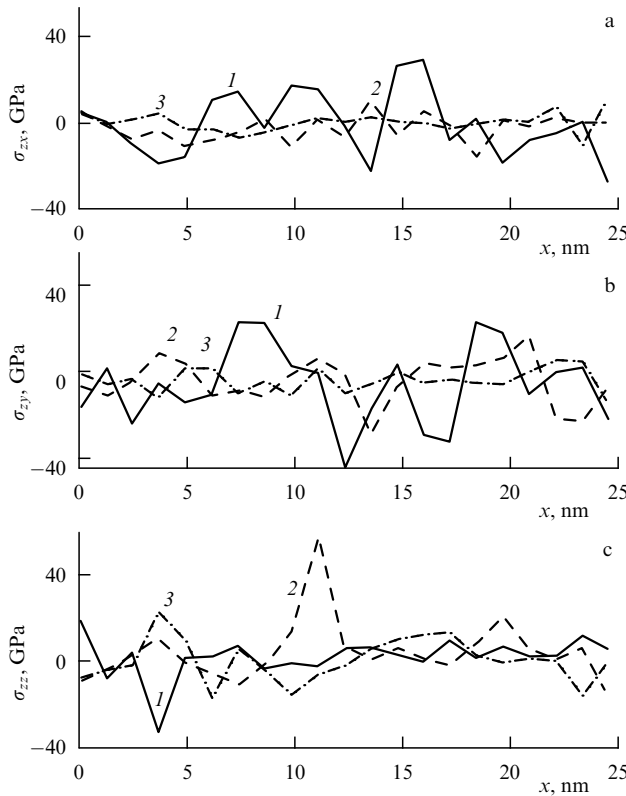


Figure 19. Distribution of stresses (a) σ_{zx} , (b) σ_{zy} , and (c) σ_{zz} in a graphene sheet over the rows of C atoms going along the armchair-edge direction at temperatures of (1) 300, (2) 1300, and (3) 3300 K in the presence of an Al film on the sheet [198].

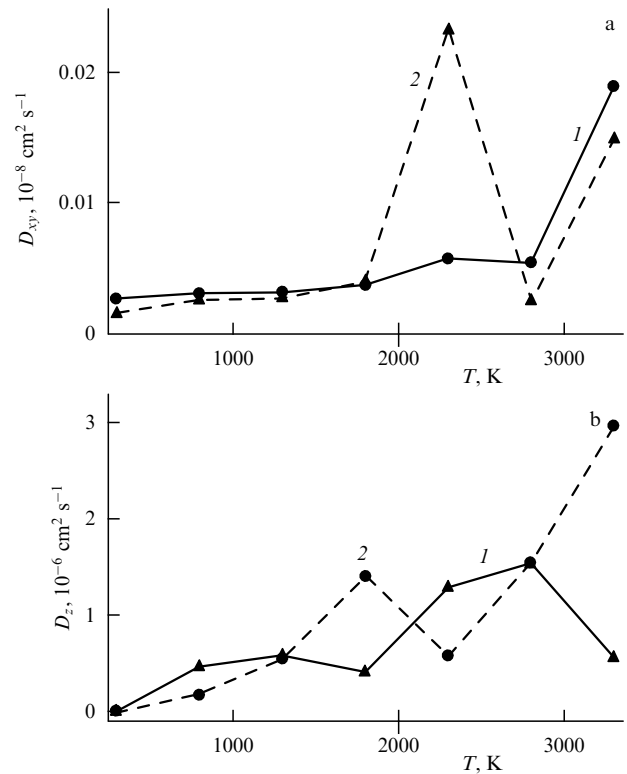


Figure 20. (a) Horizontal D_{xy} and (b) vertical D_z components of the self-diffusion coefficient for upper (1) and lower (2) sheets of graphene coated with an Al film [198].

7. Conclusions

At present, for scientific investigations and applications, a wide spectrum of allotropes of carbon and of its structural species of various dimensionalities is available. Graphene has many specific properties, owing to which it is a very useful object with great potential for application in nanotechnologies. For example, graphene is a promising material for the production of transparent flexible electrodes and nanocomposites. It is an extremely strong two-dimensional crystal with electrical properties exceeding those of silicon. The combination of these properties makes graphene an ideal material for nanoelectromechanical systems (NEMSs), which are used for controlling vibrations and accelerations. In addition, graphene possesses, apart from high strength, tunable electronic properties, chemical inertness, and high thermal conductivity, i.e., properties that are also strongly attractive from the viewpoint of various applications. Suspended graphene sheets can become the basis for almost any NEMS sensor. However, the mechanical properties of graphene sheets should be studied in much more detail, since they differ substantially from the well-known properties of bulk graphite.

The possibility was established of using graphene as an active medium for light amplification. Graphene can be used for creating wide-band optical amplifiers or high-speed modulators for telecommunications. The fabrication of membranes with pores that can be controlled on an atomic level can find wide application: for biological and chemical detection; in biotechnology (ionic and molecular methods); in power systems (batteries and fuel elements); in the field of the protection of the environment (desalination, disinfection, and decontamination of water); etc. Graphene membranes with pores on an atomic scale can be used for the investigation of gas and ion transfer.

The optical, magnetic, electrical, and electronic properties of graphene are determined by its edges. In particular, the mode in which the edges become completed, their chemical functioning, and reconstructions lead to important changes in the properties of graphene. Controlling the edges has a decisive importance for the development of applications in electronics, spintronics, and optoelectronics. Significant advances in the investigation of graphene edges achieved to date make it possible to control the morphology of the edges. However, this problem remains, as before, a fundamental one, since even insignificant deviations of the edges from the required shape significantly deteriorates the properties of the material.

There still remain many problems concerning the nanomechanics of graphene sheets. To date, Poisson's ratio of graphene has not been measured experimentally; its dependence on the number of stacked graphene sheets has not been determined. The same refers to the shear modulus of several graphene sheets separated by other substances. The mode in which these sheets slide relative to each other will make it possible to some extent to establish the mechanism of their interaction with the utilized interlayer and to determine its strength. Finally, there are many possibilities for the investigation of folds, wrinkles, and bruises of graphene sheets.

Note also the purely theoretical interest in studying the mechanical properties of graphene. For example, such investigations will make it possible to reexamine some assumptions made in the case of bulk graphite and to

eliminate uncertainties arising in the investigation of dislocations and other defects in single crystals. The results of investigations presented in this review indicate the need for further study of this unique new material.

References

1. Silva S R P et al. (Eds) *Amorphous Carbon: State of Art. Proc. of the 1st Intern. Specialist Meeting on Amorphous Carbon, SMAC'97, Cambridge, 31 July–1 August 1997* (Singapore: World Scientific, 1998)
2. Bundy F P, Kasper J S J. *Chem. Phys.* **46** 3437 (1967)
3. Goncharov A F, Makarenko I N, Stishov S M. *Sov. Phys. JETP* **69** 380 (1989); *Zh. Eksp. Teor. Fiz.* **96** 670 (1989)
4. Hanfland M, Beister H, Syassen K. *Phys. Rev. B* **39** 12598 (1989)
5. Utsumi W, Yagi T. *Science* **252** 1542 (1991)
6. Zhao Y X, Spain I L. *Phys. Rev. B* **40** 993 (1989)
7. Yagi T et al. *Phys. Rev. B* **46** 6031 (1992)
8. Mao W L et al. *Science* **302** 425 (2003)
9. Ribeiro F J et al. *Phys. Rev. B* **72** 214109 (2005)
10. Li Q et al. *Phys. Rev. Lett.* **102** 175506 (2009)
11. Umamoto K et al. *Phys. Rev. Lett.* **104** 125504 (2010)
12. Wang J-T, Chen C, Kawazoe Y. *Phys. Rev. Lett.* **106** 075501 (2011)
13. Bundy F P et al. *Carbon* **34** 141 (1996)
14. Frank I W et al. *J. Vac. Sci. Technol.* **25** 2558 (2007)
15. Lee C et al. *Science* **321** 385 (2008)
16. Bhagavantam S, Bhimasenachar J. *Proc. R. Soc. Lond. A* **187** 381 (1946)
17. Hearmon R F S. *Rev. Mod. Phys.* **18** 409 (1946)
18. Prince E, Wooster W A. *Acta Cryst.* **6** 450 (1953)
19. McSkimin H J, Bond W L. *Phys. Rev.* **105** 116 (1957)
20. McSkimin H J, Andreatch P (Jr.). *J. Appl. Phys.* **43** 2944 (1972)
21. Eletskii A V. *Phys. Usp.* **50** 225 (2007); *Usp. Fiz. Nauk* **177** 233 (2007)
22. Ivanovskii A L. *Russ. Chem. Rev.* **68** 103 (1999); *Usp. Khim.* **68** 119 (1999)
23. Brazhkin V V. *Phys. Usp.* **52** 369 (2009); *Usp. Fiz. Nauk* **179** 393 (2009)
24. Eletskii A V. *Phys. Usp.* **54** 227 (2011); *Usp. Fiz. Nauk* **181** 233 (2011)
25. Falkovsky L A. *Phys. Usp.* **55** 1140 (2012); *Usp. Fiz. Nauk* **182** 1223 (2012)
26. Varlamov A A et al. *Phys. Usp.* **55** 1146 (2012); *Usp. Fiz. Nauk* **182** 1229 (2012)
27. Li Y et al. *Carbon* **50** 566 (2012)
28. Xu Z, Buehler M J. *ACS Nano* **4** 3869 (2010)
29. Viculis L M, Mack J J, Kaner R B. *Science* **299** 1361 (2003)
30. Shioyama H, Akita T. *Carbon* **41** 179 (2003)
31. Braga S F et al. *Nano Lett.* **4** 881 (2004)
32. Shi X, Pugno N M, Gao H J. *Comput. Theor. Nanosci.* **7** 517 (2010)
33. Martins B V C, Galvão D S. *Nanotechnology* **21** 075710 (2010)
34. Bets K V, Yakobson B I. *Nano Res.* **2** 161 (2009)
35. Chuvilin A et al. *Nature Mater.* **10** 687 (2011)
36. Fujihara M et al. *J. Phys. Chem. C* **116** 15141 (2012)
37. Lim H E et al. *Nature Commun.* **4** 2548 (2013)
38. Jiang Y et al. *ACS Nano* **5** 2126 (2011)
39. Duan W H et al. *Carbon* **45** 1769 (2007)
40. Lee C et al. *Science* **321** 385 (2008)
41. Castro Neto A H et al. *Rev. Mod. Phys.* **81** 109 (2009)
42. Coluci V R et al. *Phys. Rev. B* **75** 125404 (2007)
43. Shi X et al. *Small* **6** 739 (2010)
44. Shi X et al. *Appl. Phys. Lett.* **96** 053115 (2010)
45. Li Y, Li H, Dong J, in *Innovative Graphene Technologies: Evaluation and Applications* Vol. 2 (Eds A Tiwari, A A Balandin) (Akron: Smithers Rapra Technol., 2013) p. 175
46. Xie X et al. *Nano Lett.* **9** 2565 (2009)
47. Braga S F et al. *Nano Lett.* **4** 881 (2004)
48. Chen Y, Lu J, Gao Z J. *Phys. Chem. C* **111** 1625 (2007)
49. Zhang Z, Li T. *Appl. Phys. Lett.* **97** 081909 (2010)
50. Xia D et al. *Small* **6** 2010 (2010)
51. Sessi P et al. *Nano Lett.* **9** 4343 (2009)
52. Elias D C et al. *Science* **323** 610 (2009)
53. Pujari B S et al. *Phys. Rev. B* **84** 041402(R) (2011)
54. Zhu S, Li T J. *Phys. D Appl. Phys.* **46** 075301 (2013)
55. Zhu Z et al. *Nano Lett.* **4** 2255 (2004)

56. Jin W et al. *Proc. Natl. Acad. Sci. USA* **102** 10801 (2005)
57. Yu D, Liu F *Nano Lett.* **7** 3046 (2007)
58. Sidorov A et al. *Nanotechnology* **20** 055611 (2009)
59. Bellido E P, Seminario J M *J. Phys. Chem. C* **114** 22472 (2010)
60. Patra N, Wang B, Král P *Nano Lett.* **9** 3766 (2009)
61. Heath J R *ACS Symp. Ser.* **481** 1 (1991)
62. Hunter J M et al. *J. Phys. Chem.* **98** 1810 (1994)
63. Bunshah R F et al. *J. Phys. Chem.* **96** 6866 (1992)
64. Chuvin A et al. *Nature Chem.* **2** 450 (2010)
65. Girit C Ö et al. *Science* **323** 1705 (2009)
66. Jia X et al. *Science* **323** 1701 (2009)
67. Lebedeva I V et al. *J. Phys. Chem. C* **116** 6572 (2012)
68. Ci L et al. *Nano Res.* **1** 116 (2008)
69. Iskandarov A M, Umeno Y, Dmitriev S V *Pis'ma Mater.* **1** 143 (2011)
70. Zhu T, Li J *Prog. Mater. Sci.* **55** 710 (2010)
71. Li X et al. *Phys. Rev. B* **81** 245318 (2010)
72. Pellegrino F M D, Angilella G G N, Pucci R *Phys. Rev. B* **81** 035411 (2010)
73. Pellegrino F M D, Angilella G G N, Pucci R, in *GraphITA 2011. Selected Papers from the Workshop on Fundamentals and Applications of Graphene* (Carbon Nanostructures, Eds L Ottaviano, V Morandi) (Berlin: Springer, 2012) p. 165
74. Huang M et al. *Proc. Natl. Acad. Sci. USA* **106** 7304 (2009)
75. Pellegrino F M D, Angilella G G N, Pucci R *Phys. Rev. B* **80** 094203 (2009)
76. Lee C et al. *Science* **321** 385 (2008)
77. Kim K S et al. *Nature* **457** 706 (2009)
78. Pellegrino F M D, Angilella G G N, Pucci R *Phys. Rev. B* **82** 115434 (2010)
79. Lu Q, Huang R *Int. J. Appl. Mech.* **01** 443 (2009)
80. Brenner D W et al. *J. Phys. Condens. Matter* **14** 783 (2002)
81. Lee C et al. *Science* **321** 385 (2008)
82. Yanovsky Yu G et al. *Phys. Mesomech.* **12** 254 (2009); *Fiz. Mezomekh.* **12** (4) 61 (2009)
83. Jin Y, Yuan F G *J. Nanosci. Nanotechnol.* **5** (11) 1 (2005)
84. Brenner D W *Phys. Rev. B* **42** 9458 (1990)
85. Kudin K N, Scuseria G E, Yakobson B I *Phys. Rev. B* **64** 235406 (2001)
86. Van Lier G et al. *Chem. Phys. Lett.* **326** 181 (2000)
87. Konstantinova E, Dantas S O, Barone P M V B *Phys. Rev. B* **74** 035417 (2006)
88. Tomblor T W et al. *Nature* **405** 769 (2000)
89. Jiang J-W, Wang J-S, Li B *Phys. Rev. B* **80** 113405 (2009)
90. Landau L D, Lifshitz E M *Theory of Elasticity* (Oxford: Pergamon Press, 1986); Translated from Russian: *Teoriya Uprugosti* (Moscow: Fizmatlit, 2003)
91. Krishnan A et al. *Phys. Rev. B* **58** 14013 (1998)
92. Blakslee O L et al. *J. Appl. Phys.* **41** 3373 (1970)
93. Sánchez-Portal D et al. *Phys. Rev. B* **59** 12678 (1999)
94. Zhang G, Li B *J. Chem. Phys.* **123** 114714 (2005)
95. Chang C W et al. *Phys. Rev. Lett.* **97** 085901 (2006)
96. Galashev A E, Dubovik S Yu *Phys. Solid State* **55** 1976 (2013); *Fiz. Tverd. Tela* **55** 1859 (2013)
97. Frank O et al. *ACS Nano* **4** 3131 (2010)
98. Schadler L, Galiotis C *Int. Mater. Rev.* **40** 116 (1995)
99. Hanfland M, Beister H, Syassen K *Phys. Rev. B* **39** 12598 (1989)
100. Novoselov K S et al. *Science* **306** 666 (2004)
101. Ferrari A C et al. *Phys. Rev. Lett.* **97** 187401 (2006)
102. Yu T et al. *J. Phys. Chem. C* **112** 12602 (2008)
103. Mohiuddin T M G et al. *Phys. Rev. B* **79** 205433 (2009)
104. Huang M et al. *Proc. Natl. Acad. Sci. USA* **106** 7304 (2009)
105. Tuinstra F, Koenig J L *J. Chem. Phys.* **53** 1126 (1970)
106. Thomsen C, Reich S *Phys. Rev. Lett.* **85** 5214 (2000)
107. Piscanec S et al. *Phys. Rev. Lett.* **93** 185503 (2004)
108. Galiotis C, Batchelder D N *J. Mater. Sci. Lett.* **7** 545 (1988)
109. Zhou S Y et al. *Nature Mater.* **6** 770 (2007)
110. Ribeiro R M et al. *Phys. Rev. B* **78** 075442 (2008)
111. Giovannetti G et al. *Phys. Rev. B* **76** 073103 (2007)
112. Ni Z H et al. *ACS Nano* **2** 2301 (2008)
113. Okamoto S, Ito A, in *Proc. of the Intern. MultiConf. of Engineers and Computer Scientists, IMECS 2012, March 14–16, 2012, Hong Kong Vol. 1* (Hong Kong: Newswood Ltd, 2012)
114. Matsunaga K, Iwamoto Y *J. Am. Ceramic Soc.* **84** 2213 (2001)
115. Frank O et al. *Nano Lett.* **4** 3131 (2010)
116. Tsoukleri G et al. *Small* **5** 2397 (2009)
117. Neek-Amal M, Peeters F M *Appl. Phys. Lett.* **97** 153118 (2010)
118. Tapasztó L et al. *Phys. Rev. B* **78** 233407 (2008)
119. Neubeck S et al. *Phys. Status Solidi B* **247** 2904 (2010)
120. Kowaki Y et al. *J. Phys. Condens. Matter* **21** 064202 (2009)
121. Nordlund K, Keinonen J, Mattila T *Phys. Rev. Lett.* **77** 699 (1996)
122. Hao F, Fang D, Xu Z *Appl. Phys. Lett.* **99** 041901 (2011)
123. Garaj S, Hubbard W, Golovchenko J A *Appl. Phys. Lett.* **97** 183103 (2010)
124. Krashenninnikov A V, Banhart F *Nature Mater.* **6** 723 (2007)
125. Nelayev V, Mironchik A *Mater. Phys. Mech.* **9** 26 (2010)
126. Kogeshima H et al. *Jpn. J. Appl. Phys.* **50** 070115 (2011)
127. Galashev A E, Galasheva A A *High Energy Chem.* **48** 112 (2014); *Khim. Vys. Energ.* **48** 142 (2014)
128. Lehtinen O et al. *Nanotechnology* **22** 175306 (2011)
129. Standop S et al. *Nano Lett.* **13** 1948 (2013)
130. Moliver S S, Zimagullov R R, Semenov A L *Tech. Phys. Lett.* **37** 678 (2011); *Zh. Tekh. Fiz.* **37** (14) 68 (2011)
131. Meyer J C et al. *Nano Lett.* **8** 3582 (2008)
132. Marton D et al. *Surf. Sci.* **326** L489 (1995)
133. Thrower P A, Mayer R M *Phys. Status Solidi A* **47** 11 (1978)
134. Maeta H, Iwata T, Okuda S *J. Phys. Soc. Jpn.* **39** 1558 (1975)
135. Pereira V M et al. *Phys. Rev. Lett.* **96** 036801 (2006)
136. Pereira V M, Lopes dos Santos J M B, Castro Neto A H *Phys. Rev. B* **77** 115109 (2008)
137. Peres N M R, Guinea F, Castro Neto A H *Phys. Rev. B* **73** 125411 (2006)
138. Xhie J et al. *Phys. Rev. B* **43** 8917 (1991)
139. Ouyang M, Huang J-L, Lieber C M *Phys. Rev. Lett.* **88** 066804 (2002)
140. Rutter G M et al. *Science* **317** 219 (2007)
141. Ahlgren E H, Kotakoski J, Krashenninnikov A V *Phys. Rev. B* **83** 115424 (2011)
142. Miller J C, Haglund R F (Jr.) (Eds) *Laser Ablation and Desorption* (San Diego: Academic Press, 1998)
143. Lehtinen O et al. *Phys. Rev. B* **81** 153401 (2010)
144. Wang H et al. *Nano Lett.* **12** 141 (2012)
145. Bellido E P, Seminario J J *J. Phys. Chem. C* **116** 4404 (2012)
146. Lemme M C et al. *ACS Nano* **3** 2674 (2009)
147. Bell D C et al. *Nanotechnology* **20** 455301 (2009)
148. Ziegler J F, Biersack J P, Littmark U *The Stopping and Range of Ions in Matter* (New York: Pergamon, 1985)
149. Wang Y et al. *Nano Lett.* **9** 220 (2009)
150. Yang H-X et al. *Phys. Rev. B* **84** 214404 (2011)
151. Wang W L, Meng S, Kaxiras E *Nano Lett.* **8** 241 (2008)
152. Zhang Z et al. *Phys. Rev. B* **81** 155428 (2010)
153. Nanda B R K et al. *New J. Phys.* **14** 083004 (2012)
154. Ma Y et al. *New J. Phys.* **6** 68 (2004)
155. Yazyev O V, Helm L *Phys. Rev. B* **75** 125408 (2007)
156. Zhang Y et al. *Phys. Rev. Lett.* **99** 107201 (2007)
157. Yu D et al. *Nano Res.* **1** 56 (2008)
158. Fujita M, Wakabayashi K, Nakada K *J. Phys. Soc. Jpn.* **65** 1920 (1996)
159. Klein D J *Chem. Phys. Lett.* **217** 261 (1994)
160. Jiang D, Sumpter B G, Dai S *J. Chem. Phys.* **126** 134701 (2007)
161. Hod O et al. *Nano Lett.* **7** 2295 (2007)
162. Wang Z et al. *Physica B* **405** 3895 (2010)
163. Rigo V A et al. *Phys. Rev. B* **79** 075435 (2009)
164. Ushhiro M et al. *Phys. Rev. B* **73** 144103 (2006)
165. Wang Z, Xiao J, Li M *Appl. Phys. A* **110** 235 (2013)
166. Perdew J P, Burke K, Ernzerhof M *Phys. Rev. Lett.* **77** 3865 (1996)
167. Gunlycke D et al. *Appl. Phys. Lett.* **91** 112108 (2007)
168. Wolf S A et al. *Science* **294** 1488 (2001)
169. Koskinen P et al. *Phys. Rev. Lett.* **98** 015701 (2007)
170. Koskinen P, Malola S, Häkkinen H *Phys. Rev. Lett.* **101** 115502 (2008)
171. Lee Y H, Kim S G, Tománek D *Phys. Rev. Lett.* **78** 2393 (1997)
172. Hua X et al. *Nanotechnology* **11** 85 (2000)
173. Kobayashi Y et al. *Phys. Rev. B* **73** 125415 (2006)
174. Li X et al. *Science* **319** 1229 (2008)
175. Gan Y et al. *New J. Phys.* **10** 023022 (2008)

176. Hu J, Ruan X, Chen Y P *Nano Lett.* **9** 2730 (2009)
177. Nosé S J. *Chem. Phys.* **81** 511 (1984)
178. Hoover W G *Phys. Rev. A* **31** 1695 (1985)
179. Savvatimskiy A I *Carbon* **43** 1115 (2005)
180. Zakharchenko K V et al. *J. Phys. Condens. Matter* **23** 202202 (2011)
181. Kim S G, Tománek D *Phys. Rev. Lett.* **72** 2418 (1994)
182. Zhang K, Stocks G M, Zhong J *Nanotechnology* **18** 285703 (2007)
183. Colonna F et al. *Phys. Rev. B* **80** 134103 (2009)
184. Los J H et al. *Phys. Rev. B* **72** 214102 (2005)
185. Baichi M et al. *J. Nucl. Mater.* **349** 57 (2006)
186. Ramanathan T et al. *Nature Nanotechnol.* **3** 327 (2008)
187. Rafiee M A et al. *ACS Nano* **3** 3884 (2009)
188. Titov A V, Kral P, Pearson R *ACS Nano* **4** 229 (2010)
189. Li Q Q et al. *Compos. Sci. Technol.* **69** 1193 (2009)
190. Sun Y, Chen Q F *Appl. Phys. Lett.* **95** 021901 (2009)
191. Song H Y, Zha X W *Physica B* **403** 559 (2008)
192. Song H Y, Zha X W *Commun. Theor. Phys.* **54** 143 (2010)
193. Inoue S, Matsumura Y *Chem. Phys. Lett.* **469** 125 (2009)
194. Inoue S, Matsumura Y *Chem. Phys. Lett.* **464** 160 (2008)
195. Khomyakov P A et al. *Phys. Rev. B* **79** 195425 (2009)
196. Brenner D W et al. *J. Phys. Condens. Matter* **14** 783 (2002)
197. Gao F, Bacon D J, Ackland G J *Phil. Mag. A* **67** 275 (1993)
198. Galashev A E *Tech. Phys.* **59** 467 (2014); *Zh. Tekh. Fiz.* **84** (4) 1 (2014)
199. Galashev A Y, Polukhin V A *Phys. Solid State* **55** 1733 (2013); *Fiz. Tverd. Tela* **55** 1620 (2013)
200. Galashev A Y, Polukhin V A *Phys. Solid State* **55** 2368 (2013); *Fiz. Tverd. Tela* **55** 2250 (2013)
201. Tersoff J *Phys. Rev. B* **37** 6991 (1988)
202. Tersoff J *Phys. Rev. B* **41** 3248 (1990)
203. Stuart S J, Tutein A V, Harrison J A J. *Chem. Phys.* **112** 6472 (2000)
204. Rafii-Tabar H *Phys. Rep.* **325** 239 (2000)
205. Fang T-H, Wu J-H *Comput. Mater. Sci.* **43** 785 (2008)
206. Moseler M et al. *ACS Nano* **4** 7587 (2010)