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SOLIDS AND LIQUIDS

Mobility of Vacancies under Deformation and Their Effect on the Elastic Properties of Graphene

A. S. Fedorov[a,*], D. A. Fedorov[b], Z. I. Popov[a], Yu. E. Anan'eva[b], N. S. Eliseeva[b], and A. A. Kuzubov[a,b]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*
** e-mail: alex99@iph.krasn.ru*
[b] *Siberian Federal University, Krasnoyarsk, 660028 Russia*

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Abstract—The effect of isolated vacancies on the elastic properties of a graphene sheet has been investigated by the ab initio density functional method. An almost inverse linear dependence of the Young's modulus on the concentration of vacancies has been revealed. The height of potential barriers for the motion of vacancies in various directions has been calculated as a function of various independent applied strains. The velocity of vacancies at various temperatures has been calculated as a function of applied strains using the transition state theory.

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1. INTRODUCTION

The investigation of the properties of graphene is one of the high-priority nanomaterial fields, because this material has a high mobility of electrons and holes, which is one or two orders of magnitude higher than the mobility of charge carriers in usual semiconductors, and unique strength properties. As was shown in experimental work [1], graphene is one of the most elastic and hard materials with a Young's modulus of about 1 TPa. Defects of a crystal lattice should obviously affect the electronic and elastic properties of graphene. For this reason, the structure of defects and their effect on the properties of a graphite sheet are studying by many researchers. This interest is also stimulated by, first, the use of graphite as a neutron moderator in nuclear reactors, where the formation of defects and their effect are decisive, and, second, investigation of new carbon nanostructures (assemblies of fullerenes, assemblies of carbon nanotubes, etc), which can be formed only due to sufficiently mobile defects (vacancies and multivacancies). Vacancy defects in a graphene sheet, which usually appear in the process of ion or electron bombardment of graphite or carbon nanotubes, were studied by many researchers for a long time [2–6]. Various experimental methods, viz.,—scanning tunneling microscopy [7], positron annihilation [8], and transmission electron microscopy [9], were used to study the structure and properties of vacancies in graphite and carbon nanotubes.

It was found that vacancies generated in electron-irradiated carbon nanotubes can lead to structural changes [10, 11]. Magnetic ordering on vacancies generated in proton-irradiated graphite was detected in experimental works [12, 13]. The nature of magnetism on the vacancies of lattices in graphite and graphene was theoretically studied in [14, 15] under the main assumption that vacancies in such structures are rapidly "healed" because of the fast migration of carbon adatoms on the surface, where the potential barriers for the motion of these atoms are low. However, the in situ high-resolution transmission electron microscopy investigation reported in [16] showed that vacancies in the walls of single-layer nanotubes are very stable. At the same time, the structure and diffusion of vacancies in graphene were investigated in a number of theoretical works [2, 6, 17–20]. Most of the theoretical investigations regarded the detailed structure of defects in a lattice. The dynamics of vacancies and their effect on the elastic properties of graphene, particularly for the strained state, have not yet been considered.

The aim of this work is to theoretically analyze the effect of the concentration of defects (monovacancies) in graphene on its elastic properties, as well as to study the dependence of the mobility of such vacancies on the strain of the lattice and temperature.

2. INVESTIGATION METHODS AND SAMPLES

The calculations were performed in the framework of the density functional theory (DFT) [21, 22] with the gradient corrections PBE [23] using the Vienna ab initio simulation package (VASP) [24–26]. This package is based on the pseudopotential method and the expansion of wavefunctions in the plane wave basis. This approach correctly describes periodic systems. In order to efficiently reduce the number of basis functions and to increase the calculation rate, the Vanderbilt ultrasoft pseudopotentials were used for all atoms [27]. In view of large sizes of the supercell, four k

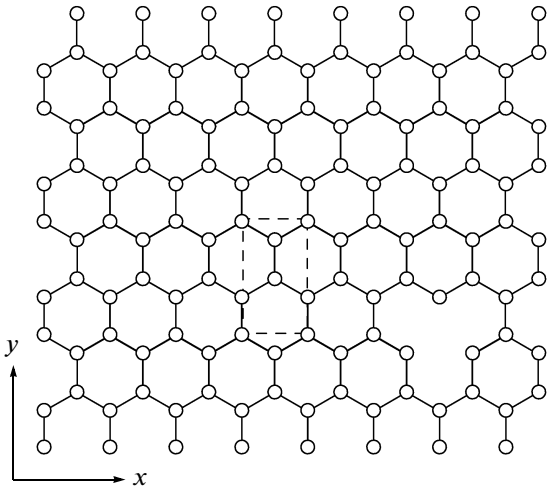

Fig. 1. Simulated graphene supercell containing 128 atoms and one vacancy. The coordinate axes are shown. The dashed contour marks the chosen rectangular unit cell.

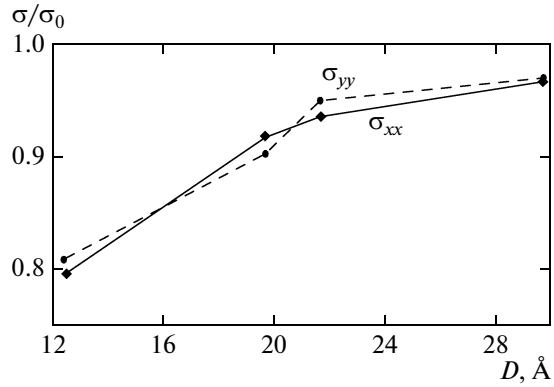

Fig. 2. Ratio of the Young's modulus σ for graphene with vacancies to the Young's modulus σ_0 for defect-free graphene in the cases of deformations along the x and y axes versus the distance D between periodic vacancies.

points in the first Brillouin zone, which were chosen by the Monkhorst–Pack scheme proposed in [28], were used to describe wavefunctions in all calculations. When optimizing the geometry, the coordinates of all atoms in the supercell were varied by the conjugate gradient method using the calculated forces acting on the atoms. The geometry was optimized until the forces acting on each atom became less than 0.05 eV/Å.

To determine the effect of vacancies on the elastic properties of graphene, we successively chose a number of supercells consisting of 60, 128, 180, and 336 carbon atoms and one defect in the form of monovacancy. All supercells are almost square in the plane with the sizes of 12.21 × 12.69, 16.54 × 16.92, 22.08 × 21.15, and 29.54 × 29.84 Å and were constructed from periodic rectangular graphene cells (see Fig. 1).

This rectangular unit cell was chosen because the independent components of the lattice strain tensor could be simulated by the compression/tension in the independent directions of the x and y axes due to the orthogonality of the basis vectors of the cell. The choice of the cell close to square ensured the equidistance of defects from each other in the x and y directions and thereby made it possible to reduce the effect of the shape of the cell on the elastic properties in these directions. The dependence of the elastic properties of the graphene sheet on the distance between defects was obtained due to the choice of various sizes of the cells. The dimension of the supercells along the z axis in all cases was 15 Å, which ensured the absence of the chemical interactions of the graphene plane with its periodically located images; a two-dimensional periodic plate with a finite thickness (slab geometry) was used.

To determine the elastic properties, we calculated the linear Young's moduli (elastic moduli) σ_{xx} and σ_{yy} for the cases of deformations in the x and y directions, respectively, for both the defect-free graphene sheet and graphene supercells containing one vacancy. For that, the supercell was successively deformed along the x and y axes by ±3 and ±6%, respectively, with respect to the initial value.

When considering fixed compression/tension along one axis, the dimension of the cell along another axis was varied by tension/compression in order to ensure zero total pressure along this axis. The calculated Young's moduli of defect-free graphene for deformations in the x and y directions are 1.02 and 0.98 TPa, respectively, which are in agreement with an experimental value of 1.0 TPa [1]. The ratios of the Young's moduli σ_{xx} and σ_{yy} for structures with a vacancy to the respective moduli for the defect-free structure are shown in Fig. 2 as functions of the distance between the vacancies (along each coordinate).

As is seen in Fig. 2, both Young's moduli of graphene with periodically located vacancies are monotonic functions of the distance between vacancies and when the distance between vacancies is $D \approx$ 30 Å, they are almost equal to the Young's moduli of the defect-free graphene sheet. The Young's moduli at the distance between vacancies $D \approx 12.5$ Å are smaller than the Young's moduli of the defect-free sheet by 20%. The intersection of the dependences under deformations along the x and y axes for small supercells is evidently due both to the nonlinearity of the interaction energy of atoms surrounding the vacancy as a function of the strain and to the interaction between vacancies located in neighboring supercells.

Further, we calculated the dependences of the mobility of vacancies in graphene on the applied strains and temperature. For that, a rectangular supercell that consists of 5 × 2 rectangular unit cells of graphene and has the sizes of 12.72 × 12.75 Å was again

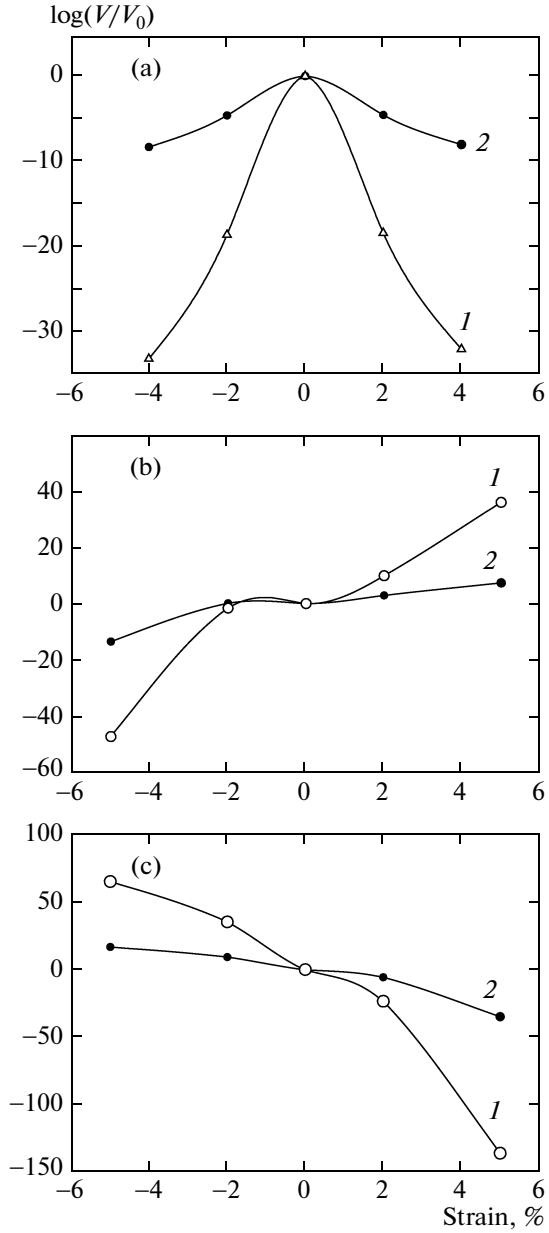

Fig. 3. Logarithm of the ratio of the diffusion rate of single vacancies in graphene to the diffusion rate in the absence of deformation versus the (a) *xy* shear strain and strains along the (b) *x* and (c) *y* axes at temperatures of (*1*) 77 and (*2*) 298 K.

chosen. One atom was removed from the supercell and, then, the geometry of the structure with a vacancy was again optimized until the forces acting on each atom became less than 0.05 eV/Å. Further, we sought the transition state (reaction path) for the hop of the nearest atom (in the *x* and *y* directions) to the vacancy position or, in other words, for the hop of the vacancy in the opposite direction.

The nudged elastic band method [29] was used to seek the transient state for the hope of the vacancy. This method allows for the calculation of the reaction path in terms of the positions of the nearest energy minima, i.e., the determination of the trajectory of the particle minimizing the total energy at each point when moving from one minimum to the neighboring one through a saddle point. For that, two extreme positions of the particle at the energy minima are connected by an imaginary expanded elastic band and the elastic energy of this band is minimized under the variation of the intermediate points of the band; this minimization procedure provides the reaction path, saddle point position, and the height of the potential barrier E_{bar}. By this method, the potential barriers for the motion of the vacancy in the *x* and *y* directions between the nearest potential energy minima were calculated. It was found that the heights of the potential barriers for the motion of the vacancies strongly depend on the applied strain. For example, the potential barrier is 1.17 eV in the absence of strain and is 1.79 and 0.12 eV at a compression strain of 5% along the *x* and *y* axes, respectively.

When the structure is strongly compressed along the *y* axis, the initial and final positions of the vacancy are sufficiently close to each other and thereby the barrier height is low. When the structure compressed along the *x* axis, the carbon atoms with broken bonds near the vacancy approach each other so close that they form a metastable compound in the form of a five-term cycle. In this case, the migration of the vacancy initiates the break of this pentagon and, as a result, increases the reaction barrier. The barriers at an expansion strain of 5% along the *x* and *y* axes are 0.75 and 3.15 eV, respectively. The barrier under shear deformation leading to change in a right angle in the unit cell by 4° is 1.66 eV. These dependences are easily explained by the fact that the barriers decrease and increase when the distance between the atoms in the nearest neighbor of the vacancy decreases and increases, respectively.

Further, the frequencies (velocities) *V* of the hop of the atom through the potential barrier E_{bar} were calculated. For that, we used the known Arrhenius-like formula

$$V = V_0 \exp(-E_{\text{bar}}/kT), \tag{1}$$

where *V* is the atom (vacancy) hopping rate. The pre-exponential factor (frequency) V_0 was calculated by the known Vineyard formula [30]

$$V_0 = \frac{kT}{\hbar}\frac{\prod_{i=1}^{3N-3}(1-\exp(-h\nu_i/kT))}{\prod_{i=1}^{3N-4}(1-\exp(-h\nu_i'/kT))}, \tag{2}$$

where ν_i' are the oscillation frequencies of *N* atoms of the system when the transferred atom is at the top of the potential barrier at the saddle point and ν_i are the oscillation frequencies of the atoms of the system

when the transferred atom is at the minimum point. Due to large size of the system, only the degrees of freedom of the transferred atom and its four nearest neighbors (free atoms), i.e., $N = 5$, were taken into account when calculating the atomic oscillation frequencies. It is worth noting that E_{bar} in Eq. (1) includes the contribution from zero atomic oscillations. This method for calculating the hopping frequencies was reported and tested in detail in our previous works [31–33].

The oscillation frequencies of the free atoms of the system were calculated by the frozen phonon method. For that, the force matrix of the system was calculated by both the deviation of each free atom by ±0.05 Å in each direction and the numerical differentiation of the forces acting on each free atom. The natural oscillation frequencies of free atoms for the wave vector $\mathbf{q} = 0$ were determined by diagonalizing the dynamic matrix calculated from the force matrix. In this procedure, the vector $\mathbf{q} = 0$ was used due to sufficiently large size of the system and, correspondingly, a weak dependence of the phonon frequencies on the wave vector.

Using the data, we plot the mobility, i.e., the hop rate of the vacancy as a function of the applied strain and temperature (see Fig. 3). It is seen that the mobility of vacancies both increases and decreases strongly (except for the shear strain) under an applied strain of up to 5%. The mobility at a temperature of 77 K changes by many orders of magnitudes in view of high potential barriers.

3. CONCLUSIONS

To summarize, the effect of single vacancies on the elastic properties of the graphene sheet has been investigated using the ab initio calculations by the pseudopotential method in the framework of the density functional theory. It has been found that the Young's moduli are inversely proportional to the vacancy concentration. The dependences of the velocity of vacancies as a function of the applied strains at various temperatures have been obtained by calculating the dependence of the height of the potential barriers for the motion of vacancies in various directions on the independent applied strains and oscillation frequencies of the nearest atoms. These dependences are of interest for experimentalists investigating graphene sheets including vacancies, because these dependences determine the conditions for the directional motion of vacancies by applying various strains or temperatures.

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