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On Using Many-Particle Interatomic Potentials to Compute Elastic Properties of Graphene and Diamond

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Abstract—The elastic properties of diatomic crystals are considered. An approach is proposed that permits calculating the elastic characteristics of crystals by using the interatomic interaction parameters specified as many-particle potentials, i.e., potentials that take into account the effect of the environment on the diatomic interaction. The many-particle interaction is given in the general form obtained in the framework of linear elastic deformation. It is shown that, by expanding in series in small deformation parameters, a group of nonlinear potentials frequently used to model covalent structures can be reduced to this general form. An example of graphene and diamond lattices is used to determine how adequately these potentials describe the elastic characteristics of crystals.

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1. INTRODUCTION

It is necessary to know the elastic characteristics of crystals in order to analyze materials, systems, and structures at nanolevel. However, quite often, many physical characteristics are known with higher accuracy than the simple mechanical properties. Such physical characteristics underlie the notion of empirical interaction potentials, which are widely used in computer simulation but often without proper analysis of the quality of modeling the elastic properties of solids. In the present paper, we use an approach that, in the framework of linear deformation, permits calculating the elastic characteristics of some crystals by using the parameters of a wide class of interaction potentials.

A crystal lattice for which the displacement by any vector connecting lattice nodes is an identical transformation is said to be simple (monatomic). Otherwise, the lattices is said to be polyatomic. In the present paper, we consider diatomic lattices, which are a special case of polyatomic lattices and can be represented as a combination of two embedded sublattices. The elementary cell of a diatomic lattice contains two atoms. As examples of such crystals, we consider graphene and diamond, whose description requires special approaches. This is due to the fact that interaction in such crystals occurs through covalent bonds, and taking account of their direction is a rather nontrivial problem. Graphene—a monolayer of a graphite lattice—was first obtained quite recently [1, 2], but the number of publications devoted to this material is enormous. This is because of its extraordinary physical properties, which potentially permit using it in electronic devices (such as field-effect transistors, nanoresonators, etc.). The mechanical properties of graphene are of interest for several reasons. First of all, creating composite materials on the basis of graphene seems to be very promising. Graphene composites are dispersed in the matrix, which then acquires increased strength, rigidity, and electro- and thermal conductivity [3]. Graphene has great potential in the production of electrodes. Finally, carbon nanotubes, which are more and more widely used in engineering and medicine, are nothing more than graphene layers wrapped

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in some way. Thus, there exist several possibilities for using the mechanical properties of graphene. Therefore, studying these properties is an important and topical problem.

The constantly increasing interest in the properties of materials with diamond structure is also caused by the development of nanotechnologies. Nanodiamonds attract attention as antifriction materials, elements of nanoelectronics, structural materials used to obtain polycrystal diamonds, abrasive materials for special purposes in surface polishing and diamond film manufacturing, and also as oil additives and for obtaining diamond-metal hardening coatings. Their use as modifiers in the production of new composites and in creating new organic materials is also in progress [4]. Moreover, there also exist several other materials having a diamond-like crystal structure (for example, silicon and germanium crystals as well as boron nitride crystals). It is difficult to overestimate their importance in micro- and nanoelectronics, and boron nitride is used as an abrasive material many of whose characteristics exceed those of diamond.

2. EXPERIMENTAL DETERMINATION OF ELASTIC PROPERTIES OF GRAPHENE AND DIAMOND

Since the van der Waals interaction of carbon atoms between layers in graphite is significantly weaker than the interatomic covalent interactions inside a layer, it seems quite obvious that the elastic properties of graphene and graphite should be similar in the reference plane. In particular, this means that the elastic moduli C_{11}, C_{22}, and C_{44} of these materials are very close to one another. The experiments with graphite performed until 1970 mainly allowed the determination of only the moduli C_{33} and C_{44} and were based on studying the compressibility and specific heat capacity of graphite [5], the methods of neutron scattering, and resonance and ultrasonic tests. The other moduli either remained undetermined at all or were determined indirectly. Apparently, the first experimental data containing the complete set of elastic properties of graphite were presented in [6]. As the object of studies, the authors considered small crystals of pyrolytic α-graphite, which have close orientations along the axis c and a large scattering of orientations along the perpendicular directions. The ultrasonic tests were used to determine the elastic constants C_{11}, C_{12}, C_{33}, and C_{44}; the methods of static compression, tension, and torsion of graphite samples were used to determine the compliance coefficients S_{11}, S_{12}, S_{13}, S_{33}, and S_{44}. The flexural free oscillations of rods were used to determine the moduli $1/S_{11}$ and C_{44}, and the shear modulus C_{44} was also determined by studying the torsional oscillations of oscillatory systems made on the basis of graphite disks. For almost forty years, these data underlay the theoretical studies of graphite and graphene as well as single-walled and multi-walled nanotubes, although other experimental studies were also performed. Pyrolytic graphite irradiated with neutrons was studied in [7]. It was discovered that the only constant that significantly differs from the data in [6] was C_{44}, although the constant C_{33} also varied slightly. Some data on pyrolytic graphite was obtained in [8] based on the methods of nonelastic neutron scattering. The dependence of elastic properties of pyrolytic graphite on pressure and temperature was investigated in [9], and an refined value of the modulus C_{44} obtained on the basis of the Mandelstam–Brillouin scattering is presented in [10]. In 2007, new data on the elastic constants of graphite was obtained by the nonelastic X-ray scattering method in [11]. The X-ray scattering overcomes the difficulties arising in neutron irradiation, specifically, the restrictions on the sample dimensions and the energy transfer, and, as compared to the ultrasonic methods, is not so sensitive to the material defect structure. A drawback of this method is the impossibility of exact determination of the coefficient C_{13} because of large structural anisotropy; however, the authors assume that this modulus is close to zero [11]. The new data is close to that given in [6] but can be assumed to be more precise, except for the modulus C_{13}.

Since, in laboratory conditions, graphene was obtained quite recently, there are not so many papers published on the experimental determination of its elastic properties. The main experimental method for studying graphene and stacks of graphene layers is the atomic force microscopy (AFM). In [12], this method is used to study the elastic properties of an object that is a stack of graphene layers (less than five) settled on a silicon dioxide substrate with grooves etched by a photolithographic method. The microscope probe presses on the graphene over a groove, the probe displacement is measured, and the measurements are used to determine the rigidity of the graphene layers. The authors associate the object under study with an elastic rod fixed at both ends and thus determine Young's modulus to be equal to 0.5 TPa. A similar approach is used in [13], where several layers of graphene are located over circular indentations on the substrate and a membrane is used as the continuum model. The membrane rigidity is determined by AFM measurements. A similar experiment was also performed with a graphene monolayer [14], and Young's modulus of the order of 1 TPa was determined as a result.

Table 1

C_{11}	C_{12}	C_{44}	K	Source
950	390	430	580	Bhagavantam and Bhimasenachar (1946), [15]
932	411	416	416	Hearmon (1946), [16]
1100	330	440	590	Prince and Wooster (1952), [17]
1076	125	576	442	McSkimin (1957), [18]
1076	275	519	542	Markham (1965), [20]
1079	124	578	442	McSkimin (1972), [19]
1076	125	577	442	Grimsditch and Ramdas (1975), [21]
1076	125	576	—	Shutilov (1980), [22]
1080	125	577	443	Gilman (2002), [23]

Thus, the differences between the data for the graphene elastic characteristics obtained by different approaches are rather significant. Apparently, the most reliable data concerning the tensile modulus was the data obtained in experiments with graphite. This is due to large errors in experiments with graphene, which are still of great interest from the standpoint of determining the flexural characteristics.

The experimental properties of diamond have been studied much better than those of graphene, but there is also a large scatter in them. Apparently, the elastic properties of diamond were first measured in 1946 using ultrasonic methods [15]. Later on, they were also measured by X-ray diffraction and precision acoustic methods (see, e.g., [16–19]). The experimental results from different sources are given in Table 1 (in GPa).

The table shows that, starting from 1957, the elastic characteristics obtained are very close, except for the data of [20] dating back to 1965.

3. MATHEMATICAL AND COMPUTER SIMULATION OF CARBON NANOSTRUCTURES

After nanotubes were discovered by Iijima [24], the study of the elastic properties of carbon compounds received a strong stimulus because the investigators predicted several unique properties of nanotubes and because modeling of new carbon compounds and materials based on them began. The nanotubes, and then other nanostructures, became the object of studies by numerous analytical and numerical methods, which were soon classified into the hierarchy of multiscale modeling [25–27]. At the lowest step of this hierarchy, which corresponds to the least dimensions and simulation times, there are ab initio methods (calculations "from first principles," the theory of the density functional). Then follow the molecular dynamics method and its generalization (the particle dynamics method), the structural methods (discrete-continuum models), and finally the continuum mechanics methods.

The particle dynamics method seems to be most natural in modeling microstructures, because each particle models an atom of the system. In this case, an important role is played by the potential determining the particle interaction. These potentials can be obtained both purely empirically and on the basis of quantum mechanical computations. For close-packed lattices, the pair potentials of force interaction such as the Lenard–Jones potential and the Morse potential can be used successfully. However, for the majority of crystals with non-close-packed lattices, this simplest model (in what follows, it will be called the force model), where the atoms are represented by material points, is insufficient. First of all, this concerns covalent crystals. However, it is the covalent bonds that are typical of many nanostructures such as graphene, fullerenes, carbon nanotubes, and organic molecules, and hence the use of paired laws of force interaction for them encounters serious difficulties related to ensuring the stability and satisfying the experimental values of elastic moduli [28]. By the way, paired interaction models can be constructed [29, 30] in choosing various laws of interaction with atoms of different coordination spheres, and such models are successfully used to solve practical problems.

Traditionally, covalent bonds are modeled by using many-particle interaction potentials that depend on the relative position of several particles (atoms). In [31, 32] and then [33, 34], it was suggested to model carbon compounds by using many-particle potentials taking account of the angles between bonds. The family of MM-potentials (in particular, the MM3-potential [35]), the AMBER

force field [36, 37], and other force fields have been effectively used to model carbon structures both abroad [38, 39] and in Russia [40].

The parameters of the above-listed potentials are chosen so as to satisfy the known physical characteristics. Most often, these are different energy and geometric characteristics of the lattice, such as the energy and the length of an interatomic bond the vacancy formation energy. The majority of the widely used force fields, such as AMBER, CHARMM, MM3, and OPLS, were developed by experts in the field of quantum and biological chemistry and were intended for the calculation of the energy forces of large molecular systems such as proteins, nucleic acid, etc. To a lesser extent, they were intended for the calculation of the mechanical properties of materials, but attempts to describe the mechanical behavior of carbon nanostructures by using these potentials can still be encountered in the literature no less frequently. An advantage of the potentials of the Tersoff–Brenner family is the fact that they were also chosen by authors so as to satisfy the elastic moduli. In [32], the potential parameters are chosen so as to satisfy the interatomic distance and the bulk modulus for diamond, and it is claimed that the potential can be used to model amorphous carbon and even graphite (graphene) with high accuracy. However, nothing is said about the method for calculating the elastic characteristics. Since the microstructures are similar, most of the methods for calculating the elastic properties developed for nanotubes can also be used for graphene. Indeed, attempts to use multi-particle potentials in such calculations were made, for example, in [42, 43]. However, these papers do not take into account that the crystal lattices under study are complex, and this results in an incorrect determination of the rigidity tensor. A overview of different potentials used to model graphene can be found in [38] and a similar overview for nanotubes is given in [39]. It follows from these papers that the values of Poisson's ratio and Young's modulus obtained by computer simulation can differ by several times.

Computer simulation is widely used to describe the properties of crystals at the microlevel. However, it is necessary to have theories that can bridge the gap between the microparameters (physical and geometric parameters of crystal lattices and parameters of effective potentials of interaction) and the macroparameters (elastic moduli, natural frequencies, etc.). To this end, it is necessary to have models, called discrete (also discrete-continuum or structural), that rely adequate description of the material microstructure. In these models, interaction at the microlevel can be described in the framework of classical mechanics (without taking into account the quantum mechanical effect), which is sufficient for studying the elastic deformation of the majority of crystalline solids. To model the interatomic interaction in crystal lattices, one must first introduce some interaction models and then, depending on the type of the model, pass to the macroscopic description of the material.

In [44], a structural approach (also called rod or discrete-continuum approach) was suggested to describe the interaction between carbon atoms. In this case, a paired force model with different interaction laws for the first and second coordination spheres was introduced. The simples (linear) interaction law is used; i.e., in fact, the interatomic bonds are replaced by linear springs with different spring constants. In the above paper and in the subsequent literature [29, 30, 38], these springs are called rods, although the flexural rigidity typical of rods is not taken into account in these models. Generally speaking, such models were also considered earlier, but it is the paper [44] that attracted attention of a wide scientific audience to this approach. In Russia, this approach was developed in [30, 45]. An obvious merit of the rod model is that a simple and descriptive mechanical analogue was suggested for carbon bonds. Therefore, it is increasingly used [29], although this model has certain drawbacks (in particular, it does not permit obtaining the correct value of Poisson's ratio for graphene [28]). Somewhat different structural models for nanostructure modeling, where the interatomic bonds are modeled by rods with flexural rigidity were suggested, in particular, in [46, 47].

Taking account of the rod flexural rigidity reflects the orientation of the covalent bond, for which the interaction forces are not central; i.e., a transverse force arises along with the longitudinal force. From the general viewpoint, such interactions can be described by taking into account the contribution of the paired moment between particles in addition to the force contribution. In this case, the potentials depend on the relative positions and rotations of two interacting particles [48–50]. In [28], it is shown that this permits removing the restriction on Poisson's ratio of graphene arising in the force model. In particular, the moment approach for modeling graphene was used in [51, 52]. An example of the moment approach used to model diamond is given in [52].

It should be noted that the continuum methods are now widely used to model nanostructures. For example, it seems quite natural to model a nanotube by an equivalent thin shell neglecting its microstructure. However, in this case, it is necessary to introduce a formal adjustable parameter that

has no physical meaning, namely, a wall thickness. When passing to the continuum theory of elasticity, the principle arbitrariness in determining the dimension of a nanoobject (in this case, its thickness) leads to an ambiguity in determining its elastic characteristics [53, 54]. For nanotubes, this phenomenon was called the "Jacobson paradox" shortly after the publication of the paper [55]. A great role in constructing continuum models is played by the anisotropy of nanoobjects [56]. Thus, in construction of continuum models, one must to take the material microstructure into account is one or another way.

Clearly, the gap between the discrete and continuum descriptions of materials is still quite large. Therefore, the potentials used in models at the microlevel are often not properly analyzed of whether they adequately describe the macro characteristics of the material In the present paper, we try to fill this gap.

4. GENERAL FORM OF RIGIDITY TENSOR OF DIATOMIC LATTICE

We consider an ideal (defect-free) complex crystal lattice. A lattice is said to be complex if there are nodes such that the displacement by the vector connecting them is not an identical transformation. We consider complex lattices whose elementary cells contain two atoms. For example, diamond, graphite, and hexagonal close-packed (HCP) crystals have such lattices. We consider the interaction only with the nearest neighbors and adjacent bonds. We denote the nearest neighbors of a given atom and the corresponding bonds by the indices α, β, and γ. We consider only the case of small linear deformations and represent the energy per volume occupied by a single atom as follows:

$$W = \frac{1}{V_0}\left[G_1\sum_{\alpha}\kappa_\alpha^2 + G_2\sum_{\alpha,\beta}{}'\xi_{\alpha\beta}^2 + G_3\sum_{\alpha,\beta}{}'(\kappa_\alpha+\kappa_\beta)\xi_{\alpha\beta} + G_4\sum_{\alpha,\beta,\gamma}{}'\xi_{\alpha\beta}\xi_{\alpha\gamma}\right]. \tag{4.1}$$

Here V_0 denotes the volume of the elementary cell, κ_α and κ_β are the strains of bonds α and β, and $\xi_{\alpha\beta}$ is the change in the angle between the bonds. The summation sign labeled with a prime denotes the summation over adjacent bonds only. It is assumed that the relations $\alpha \neq \beta \neq \gamma$ hold for each individual term.

The interaction form (4.1) containing four independent parameters G_k is quite general to be used to describe the particle interaction in the system. Many potentials in computer simulation of materials can be reduced to this form. Earlier, it was shown [57] that the form containing only two parameters (the first two terms in (4.1)) satisfies some force fields used in modeling. However, two parameters are insufficient for comparing the form of the interatomic interaction with the family of Tersoff–Brenner potentials widely used to model carbon compounds. Therefore, the form (4.1) contains two additional terms, one of which connects the bond linear strain and the change in the angle between two bonds and the other term is responsible for the change in the angles at the two bonds adjacent to the given bond. In what follows, we will show that this form completely satisfies the class of Tersoff–Brenner potentials, and hence it does not seem necessary to add terms, for example, of the form $\kappa_\alpha\kappa_\beta$ to (4.1).

If the interaction is implemented by linear springs with constant c and by angular springs with constant γ, then

$$G_1 = \tfrac{1}{2}ca^2, \quad G_2 = \tfrac{1}{2}\gamma, \quad G_3 = 0, \quad G_4 = 0, \tag{4.2}$$

where a is the length of the linear spring.

It is well known that any complex diatomic lattice can be represented as a combination of two simple sublattices. We assume that the crystal deformation is composed of homogeneous small deformations of its both sublattices. The configuration thus obtained is not in equilibrium but tends to equilibrium at the expense of a shift of one sublattice with respect to the other by a certain discrepancy vector $\boldsymbol{\zeta}$. Therefore, the strain energy, which, on one hand, is a quadratic form of the strain tensor, can be represented as a quadratic form of the strain tensor and the discrepancy vector:

$$W = \tfrac{1}{2}\boldsymbol{\varepsilon}\cdot\cdot\,{}^4\mathbf{C}\cdot\cdot\,\boldsymbol{\varepsilon} = \tfrac{1}{2}\boldsymbol{\varepsilon}\cdot\cdot\,{}^4\mathbf{C}_*\cdot\cdot\,\boldsymbol{\varepsilon} + \tfrac{1}{2}\boldsymbol{\zeta}\cdot\mathbf{C}\cdot\boldsymbol{\zeta} + \boldsymbol{\zeta}\cdot{}^3\mathbf{C}\cdot\cdot\,\boldsymbol{\varepsilon}. \tag{4.3}$$

We assume that the crystal has a uniform strain $\boldsymbol{\varepsilon}$. In this case, the discrepancy vector must ensure a shift of sublattices, at which the strain energy minimum is attained, that permits relating it to the strain tensor

$$\frac{\partial W}{\partial \boldsymbol{\zeta}} = 0 \quad \Rightarrow \quad \mathbf{C}\cdot\boldsymbol{\zeta} + {}^3\mathbf{C}\cdot\cdot\,\boldsymbol{\varepsilon} = 0 \quad \Rightarrow \quad -\mathbf{C}^{-1}\cdot{}^3\mathbf{C}\cdot\cdot\,\boldsymbol{\varepsilon}. \tag{4.4}$$

We use the last relation to express the rigidity tensor as

$$^4\mathbf{C} = {}^4\mathbf{C}_* - {}^3\mathbf{C}^T \cdot \mathbf{C}^{-1} \cdot {}^3\mathbf{C}. \tag{4.5}$$

The deformations of the bonds and angles can be represented as

$$\kappa_\alpha = \mathbf{n}_\alpha\mathbf{n}_\alpha \cdot\cdot\, \boldsymbol{\varepsilon} + \mathbf{n}_\alpha \cdot \boldsymbol{\zeta}, \quad \kappa_{\alpha\beta} = \mathbf{n}_\alpha\mathbf{n}_\beta \cdot\cdot\, \boldsymbol{\varepsilon} + \tfrac{1}{2}(\mathbf{n}_\alpha + \mathbf{n}_\beta) \cdot \boldsymbol{\zeta}, \quad \xi_{\alpha\beta} = \frac{(\kappa_\alpha + \kappa_\beta)\cos\varphi - 2\kappa_{\alpha\beta}}{\sin\varphi}. \tag{4.6}$$

We substitute formulas (4.6) into (4.1). Comparing with (4.3) and summing over three indices, we can determine the rigidity tensors of different ranks, which can be written as sums of two terms:

$$^4\mathbf{C}_* = {}^4\tilde{\mathbf{C}}_* + {}^4\hat{\mathbf{C}}_*, \quad {}^3\mathbf{C} = {}^3\tilde{\mathbf{C}} + {}^3\hat{\mathbf{C}}, \quad {}^2\mathbf{C} = {}^2\tilde{\mathbf{C}} + {}^2\hat{\mathbf{C}}. \tag{4.7}$$

Here the terms with tildes correspond to the contribution of the first three terms of (4.1) into the total rigidity tensor, and the terms with hats correspond to the contribution obtained by taking account of the adjacent angles, i.e., the last term in (4.1). With (9.12)–(9.19) we obtain

$$\begin{aligned} {}^4\tilde{\mathbf{C}}_* &= \frac{2}{V_0}\Bigg[H_1 \sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha + H_2 \sum_{\alpha,\beta}{}' \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\beta + H_2 \sum_{\alpha,\beta}{}' (\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\alpha + \mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\alpha\mathbf{n}_\beta)\Bigg], \\ {}^3\tilde{\mathbf{C}}_* &= \frac{1}{V_0} H_4 \sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha, \quad {}^2\tilde{\mathbf{C}}_* = \frac{2}{V_0} H_5 \sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha, \end{aligned} \tag{4.8}$$

where the constant coefficients H_k are expressed as

$$\begin{aligned} &H_1 = G_1 - 6M_1G_2\cot^2\varphi - 2M_1G_3\cot\varphi, \quad H_2 = 2G_2\cot^2\varphi + 2G_3\cot\varphi, \quad H_3 = 2G_2(1+\cot^2\varphi), \\ &H_4 = 2G_1 + 4G_2M_1\frac{\cot\varphi}{\sin\varphi}(1-\cos\varphi)^2 + 2G_3M_1\frac{1}{\sin\varphi}(\cos 2\varphi - \cos\varphi), \\ &H_5 = G_1 + 2G_2M_1(1-\cos\varphi) - 2G_3M_1\sin\varphi. \end{aligned} \tag{4.9}$$

We introduce the notation

$$P = \cos^2\varphi - \frac{\sin^2\varphi}{d-1}, \quad \tilde{P} = \cos^2\varphi + \frac{\sin^2\varphi}{d-1}, \quad Q = \frac{M_1M\sin^2\varphi}{d(d-1)}, \tag{4.10}$$

where M is the number of the nearest neighbors of a given atom, M_1 is the number of bonds adjacent to it, and $d = 2, 3$ is the space dimension. Then the terms responsible for taking account of the adjacent angles have the form

$$\begin{aligned} {}^4\hat{\mathbf{C}}_* &= \frac{2}{V_0}G_4\Bigg[R\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha + T\mathbf{J}_1 + U(\mathbf{J}_2 + \mathbf{J}_3)\Bigg], \\ {}^3\hat{\mathbf{C}} &= \frac{1}{V_0}G_4W\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha, \quad {}^2\hat{\mathbf{C}} = \frac{2}{V_0}G_4V\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha, \end{aligned} \tag{4.11}$$

$$\begin{aligned} R &= M_1\Bigg[(M_1-1)(1+3P)\cot^2\varphi + 4P\frac{\cot\varphi}{\sin\varphi} + 4\tilde{P}\frac{1}{\sin^2\varphi}\Bigg], \\ T &= Q\Bigg[3(M_1-1)\cot^2\varphi + 4\frac{\cot\varphi}{\sin\varphi}\Bigg], \quad U = -\frac{2Q}{\sin^2\varphi}, \\ W &= M_1(M_1-1)[2+3(P+\cos\varphi)]\cot^2\varphi - 2(M_1-1)(M_1P+1)\frac{\cot\varphi}{\sin\varphi} + \frac{4}{\sin^2\varphi}, \\ V &= M_1(M_1-1)(1+3\cos\varphi)\cot^2\varphi + (3M_1-2)\frac{\cot\varphi}{\sin\varphi}. \end{aligned} \tag{4.12}$$

By $\mathbf{J}_k$ we denote the isotropic tensors of rank four,

$$\mathbf{J}_1 = \mathbf{e}_k\mathbf{e}_k\mathbf{e}_n\mathbf{e}_n = \mathbf{E}\mathbf{E}, \quad \mathbf{J}_2 = \mathbf{e}_k\mathbf{e}_n\mathbf{e}_n\mathbf{e}_k, \quad \mathbf{J}_3 = \mathbf{e}_k\mathbf{e}_n\mathbf{e}_k\mathbf{e}_n, \tag{4.13}$$

where $\mathbf{e}_k$ are vectors of some orthonormal basis; from now on, the summation is performed over the repeated Latin index.

Formulas (4.11)–(4.12) were derived under the assumption that, for both graphene and diamond, the following relations are satisfied:

$$M_1 \cos\varphi = M_1 P = -1. \tag{4.14}$$

Formulas (4.8)–(4.12) were obtained using (9.26)–(9.31). With (9.16) and (9.19) taken into account, we obtain

$$\begin{aligned}
&{}^2\mathbf{C} = \frac{2M(H_5 + G_4 V)}{V_0 d}\mathbf{E}, \quad {}^3\mathbf{C}^T \cdot {}^3\mathbf{C} = \frac{(H_4 + G_4 W)^2}{V_0^2}\left(\frac{d+1}{d}\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha - \frac{M^2}{d^3}\mathbf{J}_1\right),\\
&{}^4\mathbf{C}_* = \frac{2}{V_0}\Big\{[H_1 + M_1 P(H_2 + 2H_3) + RG_4]\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\\
&\qquad + (H_2 Q + TG_4)\mathbf{J}_1 + (H_3 Q + UG_4)(\mathbf{J}_2 + \mathbf{J}_3)\Big\}.
\end{aligned} \tag{4.15}$$

Substituting formulas (4.15) into (4.5), we obtain the expression for the rigidity tensor of a complex lattice:

$${}^4\mathbf{C} = \kappa'\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha + \lambda'\mathbf{J}_1 + \mu'(\mathbf{J}_2 + \mathbf{J}_3), \tag{4.16}$$

$$\begin{aligned}
\kappa' &= \frac{2}{V_0}[H_1 + M_1 P(H_2 + 2H_3) + RG_4] - \frac{1}{2(H_5 + VG_4)}\frac{(H_4 + WG_4)^2}{V_0},\\
\lambda' &= \frac{2}{V_0}(QH_2 + TG_4) + \frac{(d+1)(H_4 + WG_4)^2}{2d^2(H_5 + VG_4)V_0}, \quad \mu' = \frac{2}{V_0}(QH_3 + UG_4).
\end{aligned} \tag{4.17}$$

Let us consider the tensor $\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha$. For an orthotropic material with cubic symmetry, it can be represented as [28]:

$$\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha = M_\kappa \mathbf{e}_k\mathbf{e}_k\mathbf{e}_k\mathbf{e}_k + M_\mu(\mathbf{J}_1 + \mathbf{J}_2 + \mathbf{J}_3), \tag{4.18}$$

where $\mathbf{e}_k$ are unit vectors of the cubic sublattice in the case of crystals with cubic symmetry or unit vectors of an arbitrary orthonormal basis in the case of isotropic elastic properties; M_κ and M_μ are dimensionless coefficients determined by the formulas

$$M_\kappa = 2\frac{1 - \eta_c}{d(d\eta_c + 2)}M, \quad M_\mu = \frac{\eta_c}{d(d\eta_c + 2)}M, \tag{4.19}$$

where η_c is the anisotropy parameter of the tensor $\sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha$, which coincides with the anisotropy parameter of the rigidity tensor of the material under study in the case of pure force interaction. Thus, in the anisotropic case, we have

$${}^4\mathbf{C} = \kappa\mathbf{e}_k\mathbf{e}_k\mathbf{e}_k\mathbf{e}_k + \lambda\mathbf{J}_1 + \mu(\mathbf{J}_2 + \mathbf{J}_3), \quad \kappa = \kappa' M_\kappa, \quad \lambda = \kappa' M_\mu + \lambda', \quad \mu = \kappa' M_\mu + \mu', \tag{4.20}$$

where κ, λ, μ are generalized Lamé coefficients.

In conclusion, we present the rigidity tensor for isotropic materials. In this case, we have $\eta_c = 1$, $\kappa = 0$, and

$${}^4\mathbf{C} = \lambda\mathbf{J}_1 + \mu(\mathbf{J}_2 + \mathbf{J}_3). \tag{4.21}$$

Then the Lamé coefficients become

$$\lambda = \frac{M}{d(d+2)}\kappa' + \lambda', \quad \mu = \frac{M}{d(d+2)}\kappa' + \mu'. \tag{4.22}$$

As a result, we have obtained the rigidity tensors for materials whose elementary cells of crystal lattices contains two atoms. The rigidity tensor was calculated under the assumption that only the bonds adjacent to the given bond contribute to the binding energy of two atoms. This condition is always satisfied for graphene and diamond all whose bonds are always adjacent. The elastic characteristics of these materials can be obtained from the general form of the rigidity tensor.

5. COMPUTATION OF ELASTIC CONSTANTS OF GRAPHENE AND DIAMOND

If we consider a two-dimensional isotropic material such as a graphene layer, then

$$d = 2, \quad M = 3, \quad M_\kappa = 0, \quad M_\mu = \frac{3}{8}, \quad \eta_c = 1, \quad V_0 = \frac{3\sqrt{3}}{2}a^2. \tag{5.1}$$

In this case, the elastic characteristics are calculated by the formulas:

$$C_{11} = \lambda + 2\mu, \quad C_{12} = \lambda, \quad C_{44} = \mu, \quad K = \lambda + \mu, \quad E = \frac{4\mu(\lambda+\mu)}{\lambda+2\mu}, \quad \nu = \frac{\lambda}{\lambda+2\mu}. \tag{5.2}$$

We substitute formulas (4.17) and (4.22) into (5.2) to determine the elastic characteristics of the graphene lattice as follows:

$$\begin{aligned} E &= \frac{36G_1(2G_1G_2 - G_1G_4 - G_3^2)}{V_0(G_1^2 + 18G_1G_2 - 9G_1G_4 - 6G_3^2 - 2\sqrt{3}G_1G_3)}, \\ \nu &= \frac{G_1^2 - 6G_1G_2 + 3G_1G_4 + 6G_3^2 - 2\sqrt{3}G_1G_3}{G_1^2 + 18G_1G_2 - 9G_1G_4 - 6G_3^2 - 2\sqrt{3}G_1G_3}, \quad K = \frac{3G_1}{2V_0}. \end{aligned} \tag{5.3}$$

It is easy to pass to the two-parameter model if we assume that the interaction occurs according to (4.2). Then, using the notation $c_\gamma = \gamma/a^2$, we obtain from the two-parameter model for graphene:

$$E = 8\sqrt{3}\frac{cc_\gamma}{c+18c_\gamma}, \quad \nu = \frac{c-6c_\gamma}{c+18c_\gamma}, \quad K = \frac{\sqrt{3}}{6}c. \tag{5.4}$$

An example of using a two-parameter model in graphene modeling is given in [57].

Diamond and materials with diamond-like crystal lattice (e.g., silicon and germanium) are examples of orthotropic materials with cubic symmetry. For them,

$$d = 3, \quad M = 4, \quad M_\kappa = -\frac{8}{9}, \quad M_\mu = \frac{4}{9}, \quad \eta_c \to \infty, \tag{5.5}$$

and the elastic constants can be found by the formulas

$$C_{11} = \kappa + \lambda + 2\mu, \quad C_{12} = \lambda, \quad C_{44} = \mu, \quad K = \frac{\kappa + 3\lambda + 2\mu}{3}. \tag{5.6}$$

We substitute formulas (4.17) and (4.22) into (5.6). This allows us to determine the elastic characteristics of diamond with the effect of conjugate angles between bonds taken into account:

$$\begin{aligned} C_{11} &= \frac{8}{9}\frac{G_1 + 12G_2 - 12G_4}{V_0}, \quad C_{12} = \frac{8}{9}\frac{G_1 - 6G_2 + 6G_4}{V_0}, \\ C_{44} &= \frac{16(G_1G_2 - G_3^2)}{V_0(G_1 + 8G_2 - 4G_3\sqrt{2})}, \quad K = \frac{8G_1}{9V_0}. \end{aligned} \tag{5.7}$$

The volume of the elementary cell for the diamond crystal lattice is $V_0 = 16\sqrt{3}/9a^3$, where a is the interatomic distance for carbon. Using the two-parameter model for diamond, we obtain

$$C_{11} = \frac{\sqrt{3}}{12a}(c + 12c_\gamma), \quad C_{12} = \frac{\sqrt{3}}{12a}(c - 6c_\gamma), \quad C_{44} = \frac{3\sqrt{3}}{2a}\frac{cc_\gamma}{c+8c_\gamma}, \quad K = \frac{\sqrt{3}}{12a}c. \tag{5.8}$$

As one could expect, the bulk modulus in (5.3) and (5.7) depends only on the bond tensile rigidity and is independent of the rigidities of angular interaction G_2, G_3, and G_4.

6. LINEARIZATION OF THE TERSOFF POTENTIAL BY EXPANDING IN A SERIES IN SMALL STRAINS

We represent the total energy of a system consisting of finitely many interacting atoms as

$$E = \sum_i V_i = \frac{1}{2}\sum_{i \neq j} \Pi_{ij}, \tag{6.1}$$

where the summation is performed over all atoms, V_i is the interaction energy per atom of the system, and Π_{ij} is the interatomic bond energy. The coefficient $1/2$ takes into account the fact that each bond connects two atoms. In 1988, Jerry Tersoff suggested the following form for the binding energy [31]:

$$\Pi_{ij} = f_C(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})]. \tag{6.2}$$

The indices i and j run through all interacting atoms. Here

$$f_R(r) = A\exp(-\lambda_1 r), \quad f_A(r) = -B\exp(-\lambda_2 r). \tag{6.3}$$

According to [32], we assume that for carbon atoms, interacting at distances less than 1.8Å, we have $f_C \equiv 1$ and $a_{ij} \equiv 1$. This condition holds for both graphene and diamond. The function b_{ij} has the form

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{2n}}, \tag{6.4}$$

$$\zeta_{ij} = \sum_{k\neq i,j} G(\Theta_{ijk})\exp[\lambda_3^3 (r_{ij} - r_{ik})^3], \quad G(\Theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\Theta)^2}. \tag{6.5}$$

In the above formulas, A, B, λ_1, λ_2, β, n, c, d, and h are the potential parameters that depend on the modeled material, and r_{ij} and Θ_{ijk} are the distance and the angle between the atoms specified by the subscripts.

The problem considered in this section is to linearize the Tersoff potential taking into account only the interaction between the nearest neighboring atoms and preserving the terms up to the second order of smallness inclusively. To simplify the notation, we introduce the function

$$h(x) = \exp(\lambda_3^3 x^3) \quad \Rightarrow \quad \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] = h(r_{ij} - r_{ik}). \tag{6.6}$$

We number the atoms as follows. To a given atom we assign the index 0, and to a nearest atoms, the index α. Obviously, α varies from 1 to M, where M is the number of the nearest neighbors of the given atom.

As an example, we consider one of the bonds connecting atoms 0 and 1. For this bond, we have

$$\zeta_{01} = \sum_{\beta=2}^{M} G(\Theta_{01\beta}) h(r_{01} - r_{0\beta}). \tag{6.7}$$

To simplify the notation, we omit the first index when we deal with a specific atom. So we have

$$\zeta_1 = \sum_{\beta=2}^{M} G(\Theta_{1\beta}) h(r_1 - r_\beta). \tag{6.8}$$

Thus, we can introduce the new way of designation

$$\zeta_{ij} \to \zeta_\alpha, \quad \zeta_\alpha = \sum_{\beta} G(\Theta_{\alpha\beta}) h(r_\alpha - r_\beta), \quad b_{ij} \to b_\alpha \equiv b(\zeta_\alpha^n). \tag{6.9}$$

In the above formulas, it is assumed that $j \neq i$, and the index α now specifies the bond number.

Thus, the energy of bond α for any ith atom is equal to

$$\Pi_\alpha^i = f_R(r_\alpha) + b_\alpha f_A(r_\alpha). \tag{6.10}$$

In the new notation, (6.1) takes the form

$$V_i = \frac{1}{2}\sum_{\alpha} \Pi_\alpha^i, \quad E = \sum_i V_i. \tag{6.11}$$

Since to each atom of the system there corresponds a volume equal to half the elementary cell volume, we obtain the following relation between the potential and the interaction energy:

$$W = \frac{1}{V_0}\sum_{\alpha} \Pi_\alpha. \tag{6.12}$$

Let us consider the difference

$$r_\alpha - r_\beta = a(\kappa_\alpha - \kappa_\beta), \tag{6.13}$$

where a is the initial bond length and κ_α and κ_β are the strains of the respective bonds. The strain difference is a quantity of the first order of smallness. We expand the function h in (6.6) in a series in this quantity,

$$h(r_\alpha - r_\beta) \simeq 1 + \lambda_3^3 a^3 (\kappa_\alpha - \kappa_\beta)^2. \tag{6.14}$$

The strain difference in the expansion is raised to the third degree and can be neglected compared to 1. Thus,

$$h(r_\alpha - r_\beta) \equiv 1, \quad \zeta_\alpha = \sum_\beta G(\theta_{\alpha\beta}). \tag{6.15}$$

Instead of the function G, we introduce a function g that depends on $\cos\Theta$ rather than Θ. Then we have

$$\zeta_\alpha = \sum_\beta g(\cos\Theta_{\alpha\beta}) = \sum_{\beta=2}^{M} g(\cos(\Theta_0 + \xi_{\alpha\beta})), \tag{6.16}$$

where $\Theta_0 = 2\pi/3$ for graphene and $\Theta_0 = \arccos(-1/3)$ for diamond.

Finally, we use (6.12) to determine the energy per atom of the system

$$W_i = \frac{1}{V_0}\Bigg[u_0 + u_1\sum_\alpha \kappa_\alpha + u_2 {\sum_{\alpha,\beta}}' \xi_{\alpha\beta} + G_1\sum_\alpha \kappa_\alpha^2 + G_2 {\sum_{\alpha,\beta}}' \xi_{\alpha\beta}^2 + G_3 {\sum_{\alpha,\beta}}' (\kappa_\alpha + \kappa_\beta)\xi_{\alpha\beta} + G_4 {\sum_{\alpha,\beta,\gamma}}' \xi_{\alpha\beta}\xi_{\alpha\gamma}\Bigg], \quad \alpha \neq \beta \neq \gamma. \tag{6.17}$$

Here we have used the fact that the energy of each bond of an atom (for example, of the first) can be expanded in a series in small strains preserving the second-order terms:

$$\Pi_1(r_1, \Theta_{1\alpha}) = \Pi_1(a + a\kappa_1, \Theta_0 + \xi_{1\alpha}) = \Pi_1(a, \Theta_0) + \frac{\partial\Pi_1}{\partial r_1}a\kappa_1 + \frac{\partial\Pi_1}{\partial\Theta_{12}}\sum_\alpha \xi_{1\alpha} + \frac{1}{2}\frac{\partial^2\Pi_1}{\partial r_1^2}a^2\kappa_1^2$$
$$+ \frac{\partial^2\Pi_1}{\partial r_1\partial\Theta_{12}}a\kappa_1\sum_\alpha \xi_{1\alpha} + \frac{1}{2}\frac{\partial^2\Pi_1}{\partial\Theta_{12}^2}\sum_\alpha \xi_{1\alpha}^2 + \frac{1}{2}\frac{\partial^2\Pi_1}{\partial\Theta_{1\alpha}\partial\Theta_{1\beta}}\sum_{\alpha,\beta}\xi_{1\alpha}\xi_{1\beta}, \quad \alpha\neq\beta, \quad \alpha,\beta = 2,\ldots,M. \tag{6.18}$$

Here it is taken into account that the dependence of Π_1 on Θ_α is the same for all α and assume that all the derivatives are calculated at $r_1 = a$ and $\Theta_\alpha = \Theta_0$. Similarly, we can expand the functions Π_α, where α varies from 2 to M. With (6.12) and (6.17) taken into account, we obtain

$$\begin{aligned}
&u_0 = M\Pi_1(a, \Theta_0, \Theta_0),\\
&G_1 = \frac{1}{2}\frac{\partial^2\Pi_1}{\partial r_1^2}a^2, \quad G_2 = \frac{1}{2}\left(\frac{\partial^2\Pi_1}{\partial(\cos\Theta_2)^2}\sin^2\Theta_0 - \frac{\partial\Pi_1}{\partial(\cos\Theta_2)}\cos\Theta_0\right),\\
&G_3 = -\frac{1}{2}a\frac{\partial^2\Pi_1}{\partial r_1\partial(\cos\Theta_2)}\sin\Theta_0, \quad G_4 = \frac{1}{2}\frac{\partial\Pi_1}{\partial(\cos\Theta_2)\cos\partial\Theta_3}\sin^2\Theta_0,\\
&u_1 = \frac{\partial\Pi_1}{\partial r_1}a, \quad u_2 = -\frac{1}{2}\frac{\partial\Pi_1}{\partial(\cos\Theta_2)}\sin\Theta_0.
\end{aligned} \tag{6.19}$$

When calculating these coefficients, we use the potential parameters suggested in [32]:

$$\begin{aligned}
&A = 1393.6\,\text{eV}, \quad B = 346.74\,\text{eV}, \quad \lambda_1 = 3.4879\,\text{Å}^{-1}, \quad \lambda_2 = 2.2119\,\text{Å}^{-1},\\
&\beta = 1.5724\cdot 10^{-7}, \quad n = 0.72751, \quad c = 38049, \quad d = 4.3484, \quad h = -0.57058.
\end{aligned} \tag{6.20}$$

We note that these parameters were suggested by J. Tersoff to calculate different carbon polytypes and were chosen according to the bulk modulus and interatomic binding energy of diamond. Thus,

the problem of how adequately these parameters can be used to calculate the elastic characteristics of graphene is very important. In particular, it is clear that they do not ensure an equilibrium configuration of the graphene lattice, and hence the lattice is forced to deform. Since all atoms are equivalent, the angles between bonds must remain unchanged. This implies that the only possibility for ensuring a minimum of the energy, i.e., the transition to an equilibrium configuration, is the bulk compression or extension of the lattice along interatomic bonds. We easily obtain the following condition for calculating an equilibrium bond length:

$$\left.\frac{\partial \Pi_1}{\partial r_1}\right|_{r_1=a,\Theta_{2,3}=\Theta_0=0}. \tag{6.21}$$

Thus, the equilibrium condition means that the coefficient u_1 is equal to zero, which is equivalent to the condition that the resultant of all forces acting on the body in equilibrium must be zero and must identically be satisfied for any potential.

We note that for any changes in the angles adjacent to the atom, their sum remains unchanged. This means that

$$\sum_{\alpha} \xi_\alpha = 0, \tag{6.22}$$

i.e., the coefficient u_2 always has a zero multiplier.

It follows from conditions (6.21) and (6.22) that the interaction energy (6.17) must be a quadratic form of the bond strains and changes in the angles between bonds. The term u_0 does not play any role, the derivatives of the atom energy with respect to the strains rather than the energy itself are of physical interest. Thus, we see that the form (6.17) can be reduced to the form (4.1) by using the Tersoff–Brenner-type potentials. For graphene (gr) and diamond (diam), condition (6.12) result in the following value of the bond length:

$$a_{\mathrm{gr}} = 1.46051\,\text{Å}, \quad a_{\mathrm{diam}} = 1.54396\,\text{Å}, \tag{6.23}$$

which differs from the experimental value $a_{\mathrm{gr}} = 1.42$ Å for graphene but coincides with the experimental value $a_{\mathrm{diam}} = 1.54$ Å for diamond.

Using (6.19) and taking (6.20) and (6.23) into account, we obtain the values of the desired coefficients. For graphene,

$$G_1 = 40.568\,\text{eV}, \quad G_2 = 9.2607\,\text{eV}, \quad G_3 = 3.2795\,\text{eV}, \quad G_4 = -3.7687\,\text{eV}, \tag{6.24}$$

and for diamond,

$$G_1 = 33.887\,\text{eV}, \quad G_2 = 3.3137\,\text{eV}, \quad G_3 = 3.7386\,\text{eV}, \quad G_4 = -2.7442\,\text{eV}. \tag{6.25}$$

Thus, we have used the Tersoff potential to expand the energy per atom contained in the system with respect to small parameters, the bond strains and the deformations of the angles between bonds. We have determined the coefficients of this expansion $G_1, \ldots, G_4$. These coefficients will be used in the subsequent sections to calculate the elastic characteristics of the crystal lattice.

7. LINEARIZATION OF THE FAMILY OF BRENNER POTENTIALS BY EXPANDING IN A SERIES IN SMALL STRAINS

In 1990, taking the Tersoff potential as the basis, D. Brenner suggested his potential for calculating carbon and hydrocarbon compounds [33]. The Brenner potential structure is similar to that of the Tersoff potential but differs in the form of the specific functional dependences contained. The Brenner potential was specially designed to model carbons; it became very common in the 1990s because of increasing interest in carbon nanostructures. In 2002, this potential was refined by Brenner and his colleagues so as to be used for modeling hydrocarbons [34]. In the Western literature, it was named the "second-generation Brenner potential" in contrast to the preceding first-generation potential. At present, it is the second-generation potential that is mainly used. Both potentials permit representing the energy of the bond between the ith and jth atoms as

$$\Pi_{ij} = f_R(r_{ij}) - \bar{B}_{ij} f_A(r_{ij}). \tag{7.1}$$

The functions responsible for the attraction and repulsion of atoms in the case of the first-generation potential have the form

$$f_R(r_{ij}) = \frac{D_{ij}}{S_{ij}-1}\exp\bigl[-\sqrt{2S_{ij}}\,\beta_{ij}(r_{ij}-R_{ij})\bigr],$$
$$f_A(r_{ij}) = \frac{D_{ij}S_{ij}}{S_{ij}-1}\exp\left[-\sqrt{\frac{2}{S_{ij}}}\beta_{ij}(r_{ij}-R_{ij})\right]. \tag{7.2}$$

For the second-generation potential, they are

$$f_R(r_{ij}) = f_C(r_{ij})\left(1+\frac{Q}{r_{ij}}\right)A\exp(-\alpha r_{ij}),$$
$$f_A(r_{ij}) = f_C(r_{ij})\sum_{n=1,3} B_n\exp(-\beta_n r_{ij}). \tag{7.3}$$

The symmetrized multiplier $\bar{B}_{ij}$ is responsible for changes in the angle between bonds:

$$\bar{B}_{ij} = \frac{B_{ij}+B_{ji}}{2}. \tag{7.4}$$

The multiplier B_{ij} for the first-generation potential has the form

$$B_{ij} = \left(1+\sum_{k\neq(i,j)} G_i(\Theta_{ijk})f_{ik}(r_{ik})\exp\{\lambda_{ijk}[(r_{ij}-R_{ij})-(r_{ik}-R_{ik})]\}\right)^{-\delta}, \tag{7.5}$$

$$G(\Theta) = a\left[1+\frac{c^2}{d^2}-\frac{c^2}{d^2+(1+\cos\Theta)^2}\right]. \tag{7.6}$$

For the second-generation potential, it is

$$B_{ij} = \left[1+\sum_{k\neq(i,j)} G_i(\Theta_{ijk})f_{ik}(r_{ik})\exp(\lambda_{ijk})\right]^{-1/2}. \tag{7.7}$$

The analytical form for the function $G_i(\cos\Theta_{ijk})$ is not determined; therefore it is constructed as a polynomial in the values of the function and its derivatives for the angle value $\Theta_{ijk} = 2\pi/3$ for graphene and $\Theta_{ijk} = \arccos(-1/3)$ for diamond, which are given in [34]:

$$G_{\rm gr}(\cos\Theta) = 0.05280, \quad \frac{dG_{\rm gr}}{d(\cos\Theta)} = 0.17000, \quad \frac{d^2G_{\rm gr}}{d(\cos\Theta)^2} = 0.37000,$$
$$G_{\rm diam}(\cos\Theta) = 0.09733, \quad \frac{dG_{\rm diam}}{d(\cos\Theta)} = 0.40000, \quad \frac{d^2G_{\rm diam}}{d(\cos\Theta)^2} = 1.98000. \tag{7.8}$$

In the above formulas, D_{ij}, S_{ij}, R_{ij}, A, Q, B_n, a, c, d, α, β_n, and f_C, λ_{ijk}, f_{ik} are potential parameters; they depend on the material under study. According to [33, 34], we can take $\lambda_{ijk}\equiv 0$, $f_{ij}\equiv 1$, and $f_C\equiv 1$ for graphene and diamond in the equilibrium configuration. Then the forms of the above functions, in particular, that of the multiplier B_{ij} become significantly simpler. In the reference configuration, all the angles between bonds are the same, and hence G_{ijk} is equivalent for any k, which implies $\bar{B}_{ij} = B_{ij}$. Following the method proposed in the preceding section, we pass from calculating the quantities per bond to the quantities per atom of the system. Then, by analogy with (6.10)–(6.12), we obtain

$$\Pi_\alpha = f_R(r_\alpha) - \bar{B}_\alpha f_A(r_\alpha), \quad V_i = \frac{1}{2}\sum_\alpha \Pi_\alpha, \quad E = \sum_i V_i. \tag{7.9}$$

To calculate the numerical values of the coefficients v_i in expansion (6.17) with the first-generation Brenner potential, we use the potential parameters suggested in [33] for carbon atoms:

$$R_{CC} = 1315\,\text{Å}, \quad D_{CC} = 6.325, \quad S_{CC} = 1.29, \quad \beta_{CC} = 1.5\,\text{Å}^{-1},$$
$$\delta_{CC} = 0.80469, \quad a = 0.011305, \quad c^2 = 19^2, \quad d^2 = 2.5^2. \tag{7.10}$$

Condition (6.21) implies the following value for the equilibrium bond length:

$$a_{\mathrm{gr}} = 1.45068\,\text{Å}, \quad a_{\mathrm{diam}} = 1.54055\,\text{Å}, \tag{7.11}$$

which, just as the value obtained for the Tersoff potential, differs from the experimental value for graphene (1.42 Å) but coincides with the experimental value for diamond (1.54 Å). Finally, substituting (7.10)–(7.11) into (6.17), we obtain

$$G_1 = 45.634\,\text{eV}, \quad G_2 = 1.5905\,\text{eV}, \quad G_3 = 3.1089\,\text{eV}, \quad G_4 = -0.13979\,\text{eV} \tag{7.12}$$

for graphene and

$$G_1 = 38.323\,\text{eV}, \quad G_2 = 1.0123\,\text{eV}, \quad G_3 = 3.1112\,\text{eV}, \quad G_4 = -0.16670\,\text{eV} \tag{7.13}$$

for diamond. Let us calculate the same coefficients using the parameters of the second-generation Brenner potential, which are given in [34]:

$$\begin{aligned} &B_1 = 12388.8\,\text{eV}, \quad \beta_1 = 4.72045\,\text{Å}^{-1}, \quad B_2 = 17.5674\,\text{eV}, \quad \beta_2 = 1.43321\,\text{Å}^{-1}, \\ &B_3 = 30.7149\,\text{eV}, \quad \beta_3 = 1.38269\,\text{Å}^{-1}, \quad Q = 0.313460\,\text{Å}, \quad A = 10953.5\,\text{eV}, \quad \alpha = 4.74654\,\text{Å}^{-1}. \end{aligned} \tag{7.14}$$

For these parameters, condition (6.21) implies the following value of the equilibrium bond length:

$$a_{\mathrm{gr}} = 1.42038\,\text{Å}, \quad a_{\mathrm{diam}} = 1.54401\,\text{Å}. \tag{7.15}$$

Out of the three potentials considered above, only the last one satisfies the experimental values in both cases. The expansion coefficients for graphene take the values:

$$G_1 = 43.945\,\text{eV}, \quad G_2 = 1.5601\,\text{eV}, \quad G_3 = 3.6373\,\text{eV}, \quad G_4 = -0.13773\,\text{eV}. \tag{7.16}$$

For diamond, we obtain

$$G_1 = 35.187\,\text{eV}, \quad G_2 = 4.1248\,\text{eV}, \quad G_3 = 4.4724\,\text{eV}, \quad G_4 = -0.39410\,\text{eV}. \tag{7.17}$$

Thus, it has been shown that the formulas obtained in the preceding section with the Tersoff potential can be used for any potential of the same group, in particular, for the Brenner potential. These formulas have been used to determine the coefficients of the expansion of the potential energy per atom.

8. COMPUTATION OF THE ELASTIC CHARACTERISTICS OF GRAPHENE AND DIAMOND USING THE PARAMETERS OF INTERACTION POTENTIALS

We use the formulas obtained above to calculate the elastic characteristics of graphene and diamond lattices by applying the Tersoff and Brenner potentials.

To this end, we substitute the coefficients G_k obtained in the preceding sections into (5.3) and (5.7). The numerical results for the elastic moduli of graphene are given in Table 2. Recall that they correspond to the two-dimensional theory; i.e., Young's modulus is measured in N/m, while the experimentally determined values of graphene rigidities correspond to the three-dimensional theory, and hence are measured in $\text{Pa} = \text{N/m}^2$. Therefore, the experimental characteristics have been recalculated using the known distance between the graphene layers in graphite $h = 0.34\,\text{nm}$, which is the coefficient of proportionality between the two- and three-dimensional moduli of elasticity. The volume of the three-dimensional elementary cell of a graphite crystal is equal to the product of h by the volume of the two-dimensional elementary cell of a graphene layer. In the table, we use the following notation: TP stands for the Tersoff potential, BP-1, for the first-generation Brenner potential, and BP-2, for the second-generation Brenner potential.

As follows from Table 2, the discrepancy between the experimental and theoretical data is very significant. It is paradoxical that the Tersoff potential gives a negative value of Poisson's ratio. A much better coincidence with experimental data is obtained for Young's modulus and the bulk modulus. The latter is 176 N/m for the Tersoff potential. For the first- and second-generation Brenner potentials, the bulk moduli are 201 N/m both, i.e., they are much closer to the current experimental values than the other moduli given in the table. We note that the data for the Brenner potential completely coincides with similar data given in [58], which was also obtained by comparing the energy at the micro- and macrolevels but by a somewhat different method based on the use of the continuum theory of finite strains at the macrolevel and special consideration of internal degrees of freedom at the microlevel.

Table 2

K, N/m	E, N/m	ν	Method	Source
176	407	−0.158	TP, 1988	Present paper
201	236	0.412	BP-1, 1990	Present paper
201	236	0.412	BP-1, 1990	M. Arroyo et al., 2004 [58]
194	227	0.416	BP-2, 2002	C.D. Reddy et al., 2006 [59]
201	243	0.397	BP-2, 2002	Present paper
201	243	0.397	BP-2, 2002	M. Arroyo et al., 2004 [58]
240	360	0.249	Experiment	J.C. Bowman et al., 1958 [5]
211	350	0.170	Experiment	O.L. Blakslee et al., 1970 [6]
212	371	0.125	Experiment	A. Bosak et al., 2007 [11]

Table 3

K	C_{11}	C_{12}	C_{44}	Method
426	1337	−31	566	Tersoff potential, 1988
485	664	395	230	Brenner potential-1, 1990
442	1123	101	670	Brenner potential-2, 2002
442	1079	124	578	MsSkimin (1972), [19]
442	1076	125	577	Grimsditch and Ramdas (1975), [21]
442	1076	125	576	Shutilov (1980), [22]
443	1080	125	577	Gilman (2002), [23]

Note that in [60], the results $E = 227$ N/m and $\nu = 0.416$ were obtained by a computer simulation based on the use of the second-generation Brenner potential, and these results are close to the data presented by the author of the present paper and to the data given in [58]. Moreover, in [60], the computations were performed after the minimization of the potential energy of a graphene sheet by determining an equilibrium configuration. Apparently, this resulted in a significant decrease in the error arising due to the necessity of considering the internal degrees of freedom of the lattice.

Possibly, the large error in the description of the elastic moduli by the potentials under study originates from the fact that the authors of these potentials, when trying to fit them to experimental data, did not take account of the internal degrees of freedom that correspond to shifting of sublattices in the crystal. In particular, it was shown in [58] that if Young's modulus and Poisson's ratio of graphene are calculated without taking into account the shift, then the values 337.8 N/m and 0.1580 are obtained, respectively, which are close to the experimental data. Apparently, the same result can be obtained by setting the second term in (4.5) to zero.

The numerical results for the elastic moduli of diamond are given in Table 3 (in GPa). It follows from the table that the discrepancy with the experimental data for all three potentials is significant, just as in the case of graphene. The Tersoff potential gives a negative value of the modulus C_{12}, a similar effect was also observed for graphene. The values obtained by using the second-generation Brenner potential are the closest to the experimental data and this is especially true for the bulk modulus. The first-generation Brenner potential is the most inexact; apparently, this is because Brenner did not include the constants C_{11}, C_{12}, and C_{44} in the set of experimental data used in the parametrization [59].

It follows from the above that, to describe the elastic characteristics of crystals more adequately, it is required either to refine the existing potentials or to use different approaches; for example, moment interaction should be used, whose parameters have a clear mechanical meaning, which makes it easier to ensure the correspondence between the mechanical characteristics of crystals [28, 50–52].

9. SOME RELATIONS FOR DETERMINING STRAINS OF INTERATOMIC BONDS AND COMPONENTS OF THE RIGIDITY TENSOR

In this section, we derive some relations, which were used earlier. At the first reading of the paper, this section can be omitted.

Consider the deformation of the bonds of a given particle with the nearest neighbors; let us label these bonds with the index α. In the actual configuration, the bond vectors $\mathbf{A}_\alpha$ are expressed as

$$\mathbf{A}_\alpha = \mathbf{a}_\alpha + \mathbf{u}_\alpha - \mathbf{u} + a\boldsymbol{\zeta}, \tag{9.1}$$

where $\mathbf{a}_\alpha$ is the bond vector between the given particle and particle α in the reference configuration, $\mathbf{u}_\alpha$ and $\mathbf{u}$ are the displacement vectors of particle α and the given particle, and $a\boldsymbol{\zeta}$ is the discrepancy vector (a is the bond length in the reference configuration).

Taking the long-wave approximation into account, we can write

$$\mathbf{u}_\alpha - \mathbf{u} = \mathbf{a}_\alpha \cdot \nabla\mathbf{u}. \tag{9.2}$$

Then, omitting the small terms, we obtain from (9.1):

$$\mathbf{A}_\alpha = \mathbf{a}_\alpha + \mathbf{a}_\alpha \cdot \nabla\mathbf{u} + a\boldsymbol{\zeta}, \quad A_\alpha^2 = a_\alpha^2 + 2\mathbf{a}_\alpha\mathbf{a}_\alpha \cdot\cdot\, \boldsymbol{\varepsilon} + 2\mathbf{a}_\alpha \cdot a\boldsymbol{\zeta}. \tag{9.3}$$

We express the magnitude of the bond vector in the actual configuration as

$$A_\alpha \simeq a(1 - \mathbf{n}_\alpha\mathbf{n}_\alpha \cdot\cdot\, \boldsymbol{\varepsilon} + \mathbf{n}_\alpha \cdot \boldsymbol{\zeta}). \tag{9.4}$$

Then the value of the bond strain is equal to

$$\kappa_\alpha = \frac{A_\alpha - a_\alpha}{a_\alpha} = \mathbf{n}_\alpha\mathbf{n}_\alpha \cdot\cdot\, \boldsymbol{\varepsilon} + \mathbf{n}_\alpha \cdot \boldsymbol{\zeta}. \tag{9.5}$$

Let us estimate the change in the angle φ between the bonds. Denote the small increment in the angle between bonds α and β by $\xi_{\alpha\beta}$ and write

$$\cos(\varphi + \xi_{\alpha\beta}) = \frac{\mathbf{A}_\alpha \cdot \mathbf{A}_\beta}{A^2} = \cos\varphi - \sin\varphi\,\xi_{\alpha\beta}. \tag{9.6}$$

Taking into account that $\cos\varphi = (\mathbf{a}_\alpha \cdot \mathbf{a}_\beta)/a^2$ and

$$A_\alpha \cdot A_\beta = a_\alpha \cdot a_\beta + 2\mathbf{a}_\alpha\mathbf{a}_\beta \cdot\cdot\, \boldsymbol{\varepsilon} + 2(\mathbf{a}_\alpha + \mathbf{a}_\beta) \cdot a\boldsymbol{\zeta}, \tag{9.7}$$

we arrive at the relation

$$\cos\varphi - \sin\varphi\,\xi_{\alpha\beta} = (\cos\varphi + 2\kappa_{\alpha\beta})(1 - \kappa_\alpha)(1 - \kappa_\beta). \tag{9.8}$$

Here we have introduced the notation

$$\kappa_{\alpha\beta} = \mathbf{n}_\alpha\mathbf{n}_\beta \cdot\cdot\, \boldsymbol{\varepsilon} + \tfrac{1}{2}(\mathbf{n}_\alpha + \mathbf{n}_\beta) \cdot \boldsymbol{\zeta}. \tag{9.9}$$

Transforming (9.8), we finally obtain

$$\xi_{\alpha\beta} = \frac{(\kappa_\alpha + \kappa_\beta)\cos\varphi - 2\kappa_{\alpha\beta}}{\sin\varphi}. \tag{9.10}$$

Thus, we have determined the strains of the interatomic bonds. Further, we present a method for determining the components of the rigidity tensor.

Consider the unit vectors $\mathbf{n}_\alpha$ and $\mathbf{n}_\beta$ determining the directions of two adjacent bonds. We represent $\mathbf{n}_\beta$ as the sum of two terms, parallel and perpendicular to $\mathbf{n}_\alpha$:

$$\mathbf{n}_\beta = \mathbf{n}_\alpha\cos\varphi + \mathbf{n}_a^b\sin\varphi, \tag{9.11}$$

where $\mathbf{n}_a^b$ is the unit vector perpendicular to $\mathbf{n}_\alpha$. We assume that, by the lattice symmetry, the following identities are satisfied:

$$\sum_{\beta(\alpha)} \mathbf{n}_a^b = 0, \quad \sum_{\beta(\alpha)} \mathbf{n}_a^b\mathbf{n}_a^b = \frac{M_1}{d-1}(\mathbf{E} - \mathbf{n}_\alpha\mathbf{n}_\alpha), \quad \sum_\alpha \mathbf{n}_\alpha\mathbf{n}_\alpha = \frac{M}{d}\mathbf{E}, \tag{9.12}$$

where the summation over $\beta(\alpha)$ implies the summation over all bonds adjacent to $\mathbf{n}_\alpha$; $d = 2, 3$ is the space dimension, $\mathbf{E}$ is the unit tensor corresponding to the space dimension, M is the number of the

nearest neighbors of the given atom, and M_1 is the number of the bonds adjacent to the given bond. These identities hold for the graphite lattice and also, at least, for the following crystal lattices: triangular, square, simple cubic, and BCC. Using formulas (9.11)–(9.12), we obtain

$$\sum_{\beta(\alpha)} \mathbf{n}_\beta \mathbf{n}_\beta = M_1 P \mathbf{n}_\alpha \mathbf{n}_\alpha + \frac{M_1}{d-1}\mathbf{E}, \quad P = \cos^2\varphi - \frac{\sin^2\varphi}{d-1}. \tag{9.13}$$

Then the following tensors can be transformed as

$$\begin{aligned} &\sum_{\alpha,\beta}{}' \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\beta = M_1 P \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha + Q\mathbf{J}_1, \\ &\sum_{\alpha,\beta}{}' (\mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\alpha \mathbf{n}_\beta + \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\beta \mathbf{n}_\alpha) = 2M_1 P \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha + Q(\mathbf{J}_2 + \mathbf{J}_3), \end{aligned} \tag{9.14}$$

where $\mathbf{J}_k$ are isotropic tensors of rank four,

$$\mathbf{J}_1 = \mathbf{e}_k \mathbf{e}_k \mathbf{e}_n \mathbf{e}_n = \mathbf{E}\mathbf{E}, \quad \mathbf{J}_2 = \mathbf{e}_k \mathbf{e}_n \mathbf{e}_n \mathbf{e}_k, \quad \mathbf{J}_3 = \mathbf{e}_k \mathbf{e}_n \mathbf{e}_k \mathbf{e}_n, \tag{9.15}$$

where $\mathbf{e}_k$ are the vectors of some orthonormal basis; here and henceforth, we use the summation over the repeated Latin index. We have introduced the notation

$$Q = \frac{M_1 M \sin^2\varphi}{d(d-1)}. \tag{9.16}$$

In deriving formulas for the rigidity tensor, the following useful identities will be useful:

$$\begin{aligned} &\sum_{\alpha,\beta}{}' \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha = M_1 \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha, \quad \sum_{\alpha,\beta}{}' \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha = M_1 \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha, \\ &\sum_{\alpha,\beta}{}' \mathbf{n}_\alpha \mathbf{n}_\alpha = M_1 \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha, \quad \sum_{\alpha,\beta}{}' \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\beta = M_1 \cos\varphi \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha, \\ &\sum_{\alpha,\beta}{}' \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\beta = M_1 \cos\varphi \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha, \quad \sum_{\alpha,\beta}{}' \mathbf{n}_\alpha \mathbf{n}_\beta = M_1 \cos\varphi \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha. \end{aligned} \tag{9.17}$$

Using the lattice symmetry, it is easy to see that

$$\mathbf{a}_m \cdot \mathbf{a}_n = \begin{cases} a^2, & \mu = \nu, \\ -\dfrac{a^2}{d}, & \mu \neq \nu, \end{cases} \quad \Leftrightarrow \quad \mathbf{a}_m \cdot \mathbf{a}_n = \frac{1}{d} a^2 [(d+1)\delta_{mn} - 1] \tag{9.18}$$

where δ_{mn} is the Kronecker delta. The use of formula (9.18) allows us to calculate the product

$$\sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha = \frac{d+1}{d} \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha - \frac{1}{d} \left(\sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \right) \left(\sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \right). \tag{9.19}$$

In what follows, we derive several relations that will be useful for calculating the rigidity tensor with adjacent bonds taken into account. Let us consider the terms with G_4 in (4.1):

$$\begin{aligned} \xi_{\alpha\beta}\xi_{\alpha\gamma} = {} & (\kappa_\alpha^2 + \kappa_\alpha\kappa_\beta + \kappa_\alpha\kappa_\gamma + \kappa_\beta\kappa_\gamma) \frac{\cos^2\varphi}{\sin^2\varphi} \\ & - \frac{2\cos\varphi}{\sin^2\varphi} [\kappa_{\alpha\beta}(\kappa_\alpha + \kappa_\gamma) + \kappa_{\alpha\gamma}(\kappa_\alpha + \kappa_\beta)] + \frac{4}{\sin^2\varphi} \kappa_{\alpha\beta}\kappa_{\alpha\gamma}. \end{aligned} \tag{9.20}$$

Obviously, the following relations are satisfied:

$$\begin{aligned} &\sum_{\alpha,\beta,\gamma}{}' \kappa_\alpha^2 = \sum_\alpha \kappa_\alpha^2, \quad \sum_{\alpha,\beta,\gamma}{}' (\kappa_\alpha\kappa_\beta + \kappa_\alpha\kappa_\gamma) = \sum_{\alpha,\beta} \kappa_\alpha\kappa_\beta, \quad \sum_{\alpha,\beta,\gamma}{}' \kappa_\alpha\kappa_\gamma = \frac{1}{2} \sum_{\beta,\gamma} \kappa_\beta\kappa_\gamma, \\ &\sum_{\alpha,\beta,\gamma}{}' \kappa_\alpha(\kappa_{\alpha\beta} + \kappa_{\alpha\gamma}) = \sum_{\alpha,\beta,\gamma} \kappa_\alpha\kappa_{\alpha\beta}, \quad \sum_{\alpha,\beta,\gamma}{}' \kappa_{\alpha\beta}\kappa_{\alpha\gamma} = \frac{1}{2} \sum_{\alpha,\beta,\gamma} \kappa_{\alpha\beta}\kappa_{\alpha\gamma}. \end{aligned} \tag{9.21}$$

Using them, we obtain

$$\sum_{\alpha,\beta,\gamma}{}' \xi_{\alpha\beta}\xi_{\alpha\gamma} = \cot^2\varphi\Big(\sum_{\alpha}\kappa_\alpha^2 + \sum_{\alpha,\beta}\kappa_\alpha\kappa_\beta + \frac{1}{2}\sum_{\beta,\gamma}\kappa_\beta\kappa_\gamma\Big)$$
$$- 2\frac{\cot\varphi}{\sin\varphi}\Big(\sum_{\alpha,\beta}\kappa_\alpha\kappa_{\alpha\beta} + \sum_{\alpha,\beta,\gamma}\kappa_{\alpha\beta}\kappa_\gamma\Big) + \frac{2}{\sin^2\varphi}\sum_{\alpha,\beta,\gamma}\kappa_{\alpha\beta}\kappa_{\alpha\gamma}. \tag{9.22}$$

Everything written above holds for both the two-dimensional and three-dimensional spaces.

Consider the first bracket in (9.22). Note that, for both graphite and diamond, each bond has an adjacent bond. This implies the relation

$$\sum_{\beta,\gamma}\kappa_\beta\kappa_\gamma = \sum_{\alpha,\beta}\kappa_\alpha\kappa_\beta, \tag{9.23}$$

which significantly simplifies the summation.

Let us consider the last term in (9.22). To take the symmetry of the rigidity and strain tensors into account explicitly, we use the relation

$$\kappa_{\alpha\beta}\kappa_{\alpha\gamma} = \tfrac{1}{4}(\kappa_{\alpha\beta}\kappa_{\alpha\gamma} + \kappa_{\alpha\beta}\kappa_{\gamma\alpha} + \kappa_{\beta\alpha}\kappa_{\alpha\gamma} + \kappa_{\beta\alpha}\kappa_{\gamma\alpha}). \tag{9.24}$$

Substituting relations (4.6) into (9.20) and using (9.21)–(9.24), we arrive at tensors of ranks two, three, and four, in which it is required to sum over the indices α, β, and γ. Using the lattice symmetry, we can show that, finally, it is possible to pass from the summation over two or three indices to the summation over a single index. Let us illustrate this for the required relations.

Consider the unit vectors $\mathbf{n}_\alpha$ and $\mathbf{n}_\beta$ determining the directions of two adjacent bonds. We represent $\mathbf{n}_\beta$ as the sum of two terms, parallel and perpendicular to $\mathbf{n}_\alpha$:

$$\mathbf{n}_\beta = \mathbf{n}_\alpha\cos\varphi + \mathbf{n}_a^b\sin\varphi, \quad \mathbf{n}_\gamma = \mathbf{n}_\alpha\cos\varphi - \mathbf{n}_a^b\sin\varphi, \tag{9.25}$$

where $\mathbf{n}_a^b$ is the unit vector perpendicular to $\mathbf{n}_\alpha$. Assume that, by the lattice symmetry, the following identities hold:

$$\sum_{\beta(\alpha)}\mathbf{n}_a^b = 0, \quad \sum_{\beta(\alpha)}\mathbf{n}_a^b\mathbf{n}_a^b = \frac{M_1}{d-1}(\mathbf{E} - \mathbf{n}_\alpha\mathbf{n}_\alpha), \quad \sum_{\alpha}\mathbf{n}_\alpha\mathbf{n}_\alpha = \frac{M}{d}\mathbf{E}, \tag{9.26}$$

where the summation over $\beta(\alpha)$ implies the summation over all bonds adjacent to $\mathbf{n}_\alpha$, $d = 2, 3$ is the space dimension, $\mathbf{E}$ is the unit tensor corresponding to the space dimension, M is the number of the nearest neighbors of the given atom, and M_1 is the number of the bonds adjacent to the given bond. Using formulas (9.25)–(9.26) and taking into account that

$$\sum_{\alpha,\beta}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha = M_1\sum_{\alpha}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha, \quad \sum_{\alpha,\beta}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\beta = M_1\cos\varphi\sum_{\alpha}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha, \tag{9.27}$$

we obtain the following relations:

$$\sum_{\alpha,\beta}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\beta = M_1P\sum_{\alpha}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha + Q\mathbf{J}_1,$$
$$\sum_{\alpha,\beta,\gamma}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\gamma\mathbf{n}_\gamma = \sum_{\alpha,\beta,\gamma}\mathbf{n}_\beta\mathbf{n}_\gamma\mathbf{n}_\alpha\mathbf{n}_\alpha = M_1\tilde{P}\sum_{\alpha}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha - Q\mathbf{J}_1, \tag{9.28}$$
$$\frac{1}{4}\sum_{\alpha,\beta,\gamma}(\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma\mathbf{n}_\alpha + \mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\alpha\mathbf{n}_\gamma + \mathbf{n}_\beta\mathbf{n}_\alpha\mathbf{n}_\gamma\mathbf{n}_\alpha + \mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\alpha\mathbf{n}_\gamma) = M_1\tilde{P}\sum_{\alpha}\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha - \frac{Q}{2}(\mathbf{J}_2 + \mathbf{J}_3),$$

$$P = \cos^2\varphi - \frac{\sin^2\varphi}{d-1}, \quad \tilde{P} = \cos^2\varphi + \frac{\sin^2\varphi}{d-1}, \quad Q = \frac{M_1M\sin^2\varphi}{d(d-1)}. \tag{9.29}$$

Here $\mathbf{J}_k$ denotes isotropic tensors of rank four:

$$\mathbf{J}_1 = \mathbf{e}_k\mathbf{e}_k\mathbf{e}_n\mathbf{e}_n = \mathbf{E}\mathbf{E}, \quad \mathbf{J}_2 = \mathbf{e}_k\mathbf{e}_n\mathbf{e}_n\mathbf{e}_k, \quad \mathbf{J}_3 = \mathbf{e}_k\mathbf{e}_k\mathbf{e}_k\mathbf{e}_n, \tag{9.30}$$

where $\mathbf{e}_k$ are the vectors of some orthonormal basis; here and henceforth, we use the summation over the repeated Latin index.

Proceeding similarly, we obtain the following relations for tensors of rank three:

$$\sum_{\alpha,\beta} \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\beta = M_1 P \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha, \quad \sum_{\alpha,\beta,\gamma} \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\gamma = M_1 \tilde{P} \sum_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha. \tag{9.31}$$

To derive the last relation, we have used the relation $\sum_\alpha \mathbf{n}_\alpha = 0$, which holds for many crystal lattices, in particular, for graphite and diamond.

10. CONCLUSION

In this paper, we have proposed an approach which, in the framework of linear elastic deformation, allows one to uniquely connect the elastic characteristics of graphene and diamond with the parameters of several widely known interaction potentials. This approach has been tested by the calculation of the elastic characteristics of graphene using the Tersoff and Brenner parameters. The moduli thus obtained are in a good agreement with the data obtained by other investigators using different methods for calculating the elastic characteristics on the basis of the same potentials. An advantage of the approach proposed in the present paper is the possibility to calculate the elastic characteristics of diamond in addition to those of graphene. The calculated elastic moduli significantly differ from the experimental values. Thus, the interaction potentials proposed by Tersoff and Brenner, when applied to problems of mechanics, can be used to obtain qualitative estimates but cannot pretend to give quantitative results. There are several reasons for this. Firstly, the potentials are very difficult to parameterize; it is often impossible to choose parameters so as to satisfy different materials with good accuracy. Secondly, the potentials do not allow one to taking account of the internal degrees of freedom (shift of sublattices) in model calculations in a correct way. Without any doubt, this does not depreciate the merits of the work by Tersoff, Brenner, and their colleagues. The breakthrough in the field of computational physics caused by these potentials is very significant. At the same time, it is necessary to deal very carefully with the quantitative estimates of the mechanical characteristics obtained with these potentials. For researchers in mechanics, the importance of the approach proposed in the present paper is that it permits adjusting the potential parameters so as to obtain better agreement with the experimental data.

This approach has been developed in the framework of studying adjacent bonds. For graphene and diamond lattices all whose bonds are adjacent, this assumption is justified. Apparently, for other diatomic lattices not all of whose bonds are adjacent (for example, for hexagonal closely packed and FCC lattices), this approach can also be used, but one should pay special attention to the estimation of the errors arising in this case. Moreover, as was noted in the preceding section, if, in the expression for the rigidity tensor, we omit the term related to the internal degrees of freedom, then the above methods can be used to calculate the elastic properties of simple lattices.

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