

Description for Mechanical Properties of Graphene Using Particles with Rotational Degrees of Freedom

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The unique mechanical properties of graphene [1] offer wide possibilities for its practical application in various fields of science and engineering. In particular, graphene is currently used in development and production of nanoresonators [2]. Therefore, an urgent problem is the development of models for description of the mechanical properties of graphene and other carbon nanostructures under various loadings. In practice, the mechanical behavior of carbon structures is often simulated using discrete-continuum models [3, 4]. Thermal motion can be taken into account explicitly by the molecular dynamics method [5] based on integration of classical equations of motion of interacting particles. Within molecular dynamics simulation, the key role is played by the laws of interatomic between particles (interatomic potentials). In the case of graphene, construction of such potentials is complicated due to the fact that interatomic bonds are directed. This problem is often solved using many-body potentials, which depend on the positions of a large number of particles [6, 7]. These potentials describe the physicochemical properties of graphene with high accuracy. However, the mechanical properties are reproduced, as a rule, with a large error [8]. The literature review [8] show that the overwhelming majority of the known many-body potentials describe elastic moduli (in particular, Poisson's coefficient) of graphene incorrectly. According to the results reported in [8, 9], the mechanical properties of graphene are described most accurately by the AIREBO potential (see table) [7].

An alternative approach based on the moment interactions is described, for example, in [10]. It was

shown that, at an appropriate choice of interaction parameters, the elastic properties of graphene in the sheet plane can be reproduced accurately. In study [10], however, building the potential describing strong deformation and fracture is not discussed. The use of such a potential for description of in-plane properties of graphene was proposed in [11] and generalized to the three-dimensional case in [12]. However, the potential proposed in [12] cannot be used at large relative rotations of particles during strong deformation and fracture of graphene.

This study was aimed at development of the approach described in [10]. The main relations are presented that describe the interactions of particles with rotational degrees of freedom; the approaches proposed in [10, 5] are combined. These relations are used to build the potential for carbon in the sp^2 hybridization state. The connection between parameters of

Mechanical characteristics of graphene. Experimental data and results of the molecular-dynamic simulations

Parameter	Potential (4)	Potential AIREBO [9]	Experimental [data]
E , N/m	346.5	338	350 [13]
ν	0.171	0.21	0.17 [13]
$\sigma_{cr}(\text{zigzag})$, N/m	45.8	43	42* [1]
$\sigma_{cr}(\text{armchair})$, N/m	42.6	34	42* [1]
$\varepsilon_{cr}(\text{zigzag})$	0.196	0.20	0.25* [1]
$\varepsilon_{cr}(\text{armchair})$	0.186	0.13	0.25* [1]
K_B , nN nm	0.225	0.225**	—
Error	$\leq 1\%$	$\leq 5\%$	$\leq 20\%$

* Strength properties of graphene were considered to be isotropic [1].

** The value of bending stiffness was calculated in [15] on the basis of the first-generation Brenner potential.

the potential and characteristics of an interatomic bond is determined. Molecular-dynamic simulation of deformation and fracture of graphene upon tension is performed. During simulation, elastic and strength characteristics of graphene are calculated. The obtained values are compared with the known experimental data [1, 13] and the results of the molecular-dynamic simulation on the basis of the many-body AIREBO potential [9].

We build the potential describing the interatomic interactions in graphene using the approaches proposed in [10, 5]. We use a point rigid body as a model of the carbon atom [10]. For brevity, hereinafter the point solids are referred to as particles. Let the interactions between particles be implemented by forces and moments that depend on the mutual position and orientation of particles. In this study, we limit our consideration solely to pair interactions [10]. Our argumentation is demonstrated by the example of two particles marked with indices 1 and 2. Let us introduce the following notation: \underline{F}_i and \underline{M}_i are the force and moment affecting the i th particle from the side of the second particle; moment \underline{M}_i is calculated relative to the i th particle. The values of \underline{F}_i and \underline{M}_i satisfy Newton's third law for the forces, analogue of Newton's third law for the moments and the energy balance equation [10]:

$$\begin{aligned} \underline{F}_1 &= -\underline{F}_2 \stackrel{\text{def}}{=} \underline{F}, & \underline{M}_1 + \underline{M}_2 - \underline{r}_{12} \times \underline{F} &= 0, \\ \dot{U} &= \underline{F} \cdot \dot{\underline{r}}_{12} - \underline{M}_1 \cdot \underline{\omega}_1 - \underline{M}_2 \cdot \underline{\omega}_2, \end{aligned} \quad (1)$$

where $\underline{r}_{12} \stackrel{\text{def}}{=} \underline{r}_2 - \underline{r}_1$, \underline{r}_i is the radius-vector of the i th particle, ω_1 and ω_2 are the angular velocities of particles, and U is the internal energy of the system. Let us determine the correlation of the forces and moments in the system of two particles with the internal energy. For this purpose, we introduce two sets of unit vectors $\{\underline{n}_1^j\}_{j \in \Lambda_1}$ and $\{\underline{n}_2^j\}_{j \in \Lambda_2}$ that tightly bond with particles 1 and 2, respectively, where Λ_1 and Λ_2 are the index sets. Let the introduced vector sets be such that they can completely specify the orientation of the particles. The maximum number of vectors is not limited and does not affect our consideration. In the general case, U depends on the position and orientation of the particles. Let the orientation of a particle be unambiguously specified by vectors $\{\underline{n}_1^j\}_{j \in \Lambda_1}$ and $\{\underline{n}_2^j\}_{j \in \Lambda_2}$; then, we may write

$$U = U(\underline{r}_{12}, \{\underline{n}_1^j\}_{j \in \Lambda_1}, \{\underline{n}_2^j\}_{j \in \Lambda_2}). \quad (2)$$

Using formula (2) and energy balance equation (1) and assuming that forces \underline{F}_i and moments \underline{M}_i do not depend on the linear and angular velocities of the particles, it can easily be shown that

$$\underline{F} = \frac{\partial U}{\partial \underline{r}_{12}}, \quad \underline{M}_i = \sum_{j \in \Lambda_i} \frac{\partial U}{\partial \underline{n}_i^j} \times \underline{n}_i^j, \quad i = 1, 2. \quad (3)$$

If internal energy (2) is known, formulas (3) determine the expressions for the forces and moments necessary for the molecular-dynamic simulation. Function U should satisfy the material objectivity principle. Note also that, in the case when the internal energy is objective, the forces calculated by formulas (3) automatically satisfy Newton's third law for moments. Hereinafter, function U is referred to as the interatomic potential.

On the basis of the above approach, we build the potential describing the covalent interactions between carbon atoms in the sp^2 hybridization state. We seek the potential in the form

$$U = U(\underline{r}_{12}, \{\underline{e}_{12} \cdot \underline{n}_1^j\}_{j \in \Lambda_1}, \{\underline{n}_1^j \cdot \underline{n}_2^k\}_{j \in \Lambda_1, k \in \Lambda_2}),$$

where $\underline{e}_{12} \stackrel{\text{def}}{=} \frac{\underline{r}_{12}}{r_{12}}$. To obtain the required symmetry of interactions in graphene, we choose the vectors related to the particles as follows. Let the unit vectors \underline{n}_i^j ($j = 1, 2, 3, 4$) be related to the i th particle. We place vectors \underline{n}_i^1 , \underline{n}_i^2 , and \underline{n}_i^3 in one plane by the angles $2\pi/3$ to one another (this is analogous to arrangement of the bonds in a strainless graphene sheet). Vector \underline{n}_i^4 is determined by the relation $\underline{n}_i^4 = \frac{2\underline{n}_i^1 \times \underline{n}_i^2}{\sqrt{3}}$. For the interactions to be symmetrical, we require the potential to be invariable upon permutation of vectors \underline{n}_i^1 , \underline{n}_i^2 , and \underline{n}_i^3 and upon the replacement $\underline{n}_i^4 \rightarrow -\underline{n}_i^4$. We also require the bonds in graphene to have stiffness in tension/compression, shear, bending, and torsion [10]. According to the above general considerations, we express the energy of the interaction between particles 1 and 2 as

$$\begin{aligned} U &= \varphi_R(r_{12}) + \varphi_A(r_{12})(U_B + U_T), \\ U_B &= \sum_{j,k=1}^3 \eta(\underline{n}_1^j \cdot \underline{n}_2^k) [\psi(\underline{e}_{12} \cdot \underline{n}_1^j) + \psi(\underline{e}_{21} \cdot \underline{n}_2^k)], \\ U_T &= U_T(\underline{n}_1^4 \cdot \underline{n}_2^4, \underline{e}_{12} \cdot \underline{n}_1^4, \underline{e}_{21} \cdot \underline{n}_2^4). \end{aligned} \quad (4)$$

Functions φ_A and φ_R describe attraction/repulsion between the particles, and U_B and U_T provide bond resistance against shear, bending, and torsion. We choose the functions in formula (4) to satisfy exactly the following parameters of the interatomic bond: bond energy D ; longitudinal, transversal, bending, and torsion stiffnesses c_A , c_D , c_B , and c_T [10]; critical bond length (i.e., the distance corresponding to the maximum force arising between particles upon bond

stretching) b ; and the nonlinearity coefficient $k_* \stackrel{\text{def}}{=} \frac{c_A(b-a)}{f_*}$, where f_* is the bond strength. In addition, we require the considered functions to be smooth along with their first derivatives. This ensures continuity of the forces and moments (3). The set of the functions satisfying these requirements is

$$\varphi_A(s) = \begin{cases} B_1 + B_2(s-a)^2 \left(1 + B_3 \frac{s-a}{b-a} + B_4 \frac{(s-a)^2}{(b-a)^2} \right), & s \in [0; b], \\ B_5 + B_6(s-b) \left(1 - B_7 \left[4 \frac{(s-b)^2}{a^2} + \frac{(s^2-b^2)^6}{a^{12}} \right] \right), & s \in [b; a_{cut}]; \end{cases} \quad (5)$$

$$\varphi_R(s) = B_2 B_4 \frac{a^{10}}{s^{12}} (s-a)^4, \quad s \in [0; a];$$

$$\psi(s) = s^2 \left(\frac{1}{2} + B_8(s-1) \right), \quad s \in [0; 1];$$

$$\eta(s) = s^2 (1 + B_9(s+1)), \quad s \in [-1; 0];$$

$$U_T(s_1, s_2, s_3) = B_{10}((s_1 + s_2 s_3)^2 (1 + s_2^2)(1 + s_3^2) - 1),$$

where a is the equilibrium distance and a_{cut} is the cutoff radius. An important feature of functions (5) is that parameters B_i entering these functions are fairly simply expressed by the mechanical characteristics of the interatomic bond. It can be shown that the expressions for B_i have the form

$$B_1 = -D, \quad B_2 = \frac{c_A}{2}, \quad B_3 = \frac{2(3-2k_*)}{3k_*}, \quad B_4 = \frac{k_*-2}{2k_*},$$

$$B_5 = -D + \frac{c_A(b-a)^2(k_*+6)}{12k_*}, \quad B_6 = \frac{c_A(b-a)}{k_*}, \quad (6)$$

$$B_8 = \frac{c_D a^2}{2D} - 1,$$

$$B_9 = \frac{c_D a^2}{4D} - \frac{c_B}{D} + 2, \quad B_{10} = \frac{c_T}{2D}.$$

It is seen from formulas (6) that, by fitting the parameters of potential (5), the values of D , a , b , c_A , c_D , c_B , c_T , and k_* characterizing the interatomic bonds in graphene can be satisfied exactly. The properties of the interatomic bonds determine, in turn, the mechanical properties of graphene on the macroscale. In particular, it was shown in [10, 14] that the values of c_A , c_D , c_B , c_T unambiguously determine the elastic moduli of graphene (Young's modulus, Poisson's coefficient, and bending stiffness). Within the proposed model, bending and shear rigidities of the bond, c_B and c_D , are independent. Note that, in the widely used rod models of graphene [4], the relation $c_B = c_D a^2/12$ is found.

Quantities k_* and b are uniquely related to the strength and critical deformation of graphene upon tension. In this study, we used the following values of the characteristics of the carbon–carbon bond:

$$D = 0.7899 \text{ nN nm}, \quad a = 0.1430 \text{ nm},$$

$$b = 0.1859 \text{ nm}, \quad k_* = 3.100, \quad c_A = 800.0 \text{ N/m}, \quad (7)$$

$$c_D = 396.0 \text{ N/m}, \quad c_B = c_T = 0.3902 \text{ nN nm}.$$

The values of D and a were taken from [6, 10]. Longitudinal and transversal bond stiffness c_A and c_D were determined in a series of the molecular-dynamic experiments on uniaxial deformation of graphene at the temperature of 300 K. In the simulation, the following set of equations of motion was solved numerically:

$$m \dot{\underline{v}}_i = \sum_{j \neq i} \underline{F}_{ij}, \quad J \dot{\underline{\omega}}_i = \sum_{j \neq i} \underline{M}_{ij}, \quad (8)$$

where m and J are the mass and moment of inertia of a particle (for simplicity, the particles were assumed to have a spherical tensor of inertia). Forces \underline{F}_{ij} and moments \underline{M}_{ij} affecting the i th particle from the side of the j th particle were calculated on the basis of potential (4) by formulas (3). In the simulation, Young's modulus E and Poisson's coefficient ν of graphene were calculated. The values of c_A and c_D were chosen from the condition of the best correspondence between the simulation and experimental elastic moduli [1]. Note that the values of c_A and c_D used in this study differ from the values from [10] ($c_A = 730 \text{ N/m}$ and $c_D = 402 \text{ N/m}$) by 10%, since in [10] thermal motion was not taken into account. Parameters c_B and c_T were chosen from the correspondence of bending stiffness of a graphene sheet determined by potential (4) and the results of the calculation on the basis of the first-generation Brenner potential [15]. In this study, the bending stiffness was determined as [14]

$$K_B = \frac{\sqrt{3} c_B (c_B + 3c_T)}{6 c_B + c_T}.$$

To determine bond strength characteristics b and k_* , the molecular-dynamic simulation of the uniaxial tension of a graphene sheet in the zigzag and armchair directions was performed. In the simulation, strength limit σ_{cr} and critical deformation ε_{cr} were determined. Parameters b and k_* were chosen from the condition of best consistency between the calculated and experimental data [1]. The molecular-dynamic simulation

resulted in the following values of the parameters of potential (4):

$$\begin{aligned}
 B_1 &= -0.7899 \text{ nN nm}, & B_2 &= 400.0 \text{ N/m}, \\
 B_3 &= -0.6882, & B_4 &= 0.1774, \\
 B_5 &= -0.4297 \text{ nN nm}, & B_6 &= 11.07 \text{ nN}, \\
 B_7 &= 0.1421, & B_8 &= 4.1260, \\
 B_9 &= 4.069, & B_{10} &= 0.2470, & a_{cut} &= 0.2325 \text{ nm}, \\
 J &= 0.01 \text{ m a}^2, & m &= 19.92 \times 10^{-21} \text{ g}.
 \end{aligned}
 \tag{9}$$

Parameters B_7 and a_{cut} characterizing the long-range character of the potential were found by solving the set of equations $\varphi_R(a_{cut}) = 0$ and $\varphi'_A(a_{cut}) = 0$. The values of the mechanical characteristics of graphene obtained in the simulation and the results of the calculation on the basis of the AIREBO potential [11] and the experimental data [1, 13] are presented in the table. It can be seen that the values of the mechanical characteristics of graphene are in good agreement with the experimental data from [1, 13] and the results of the calculation on the basis of the AIREBO potential [11]. The values of the elastic moduli differ from the experimental data from [13] by no more than 1%. Strength characteristics coincide with the experimental data from [1] accurate to the experimental error. Note also that, unlike the AIREBO potential, potential (4) makes it possible to satisfy the experimental Poisson coefficient from [13] accurately.

Thus, potential (4) proposed in this study allows to describe the elastic and strength properties of graphene within the experimental error.

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