Description of elastic properties of diamond using angular atomic interaction

S. S. Khakalo A. M. Krivtsov O. S. Loboda
akrivtsov@bk.ru

Abstract

Model of diamond taking into account angular interaction between its atoms is presented. Formulae representing the stiffness tensor in terms of the parameters of angular atomic interaction are derived. Obtained results are compared with the experimental data. Comparison with the model based on the moment atomic interaction is made.

1 Description of the model. Derivation of the coefficients

Diamond is one of the allotrope forms of carbon, mineral with a complex crystal structure. Diamond is orthotropic material so it has 3 mutual perpendicular planes of symmetry. The scheme of the diamond crystal is shown in Fig. 1 where cube faces act as planes of symmetry.

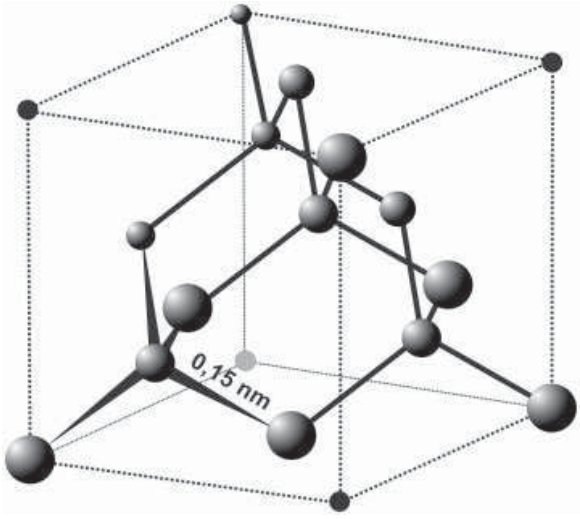

Figure 1: Fragment of the diamond crystal lattice.

Let us consider model of the diamond lattice, depicted in Fig. 2. It represents the ideal biatomic crystal lattice, which atoms are located in the center and vertices of a perfect tetrahedron.

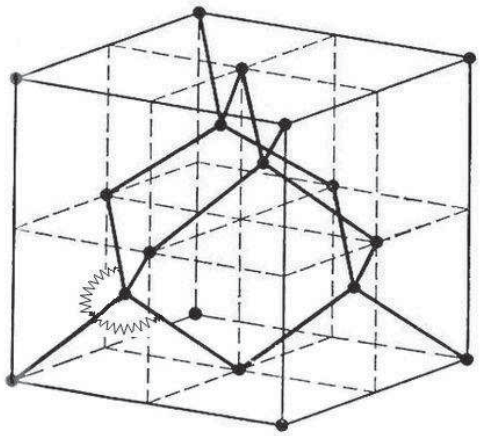

Figure 2: Model of the diamond lattice.

Interaction between atoms are described using longitudinal springs with stiffness c and angular springs with stiffness γ. The elementary cell of such lattice contains two atoms. These atoms are named as atoms of the first and second type. Atoms of each type form a simple crystal lattice, and these lattices are congruent. We choose one of the atoms of the first type as a reference atom. It is postulated that each atom interacts only with the nearest ones. From fig. 2 it is seen that each atom is surrounded by 4 nearest neighbours. Corresponding interactions are numbered from 1 to 4. Let us use an orthonormal basis with vectors perpendicular to the planes of symmetry of the lattice. Then the unit vectors directed to the nearest atoms can be represented as:

$$\mathbf{n}_1 = \frac{1}{\sqrt{3}}(\mathbf{i}-\mathbf{j}+\mathbf{k}), \qquad \mathbf{n}_2 = \frac{1}{\sqrt{3}}(-\mathbf{i}+\mathbf{j}+\mathbf{k})$$
$$\mathbf{n}_3 = \frac{1}{\sqrt{3}}(\mathbf{i}+\mathbf{j}-\mathbf{k}), \qquad \mathbf{n}_4 = \frac{-1}{\sqrt{3}}(\mathbf{i}+\mathbf{j}+\mathbf{k}).$$

In the work [1] the following formulae for an orthotropic material were obtained:

$$^4\mathbf{C} = \kappa \mathbf{e}_k\mathbf{e}_k\mathbf{e}_k\mathbf{e}_k + \lambda \mathbf{J}_1 + \mu \mathbf{J}_{23}, \tag{1}$$

where

$$\mathbf{J}_1 \overset{\text{def}}{=} \mathbf{e}_k\mathbf{e}_k\mathbf{e}_n\mathbf{e}_n, \qquad \mathbf{J}_{23} \overset{\text{def}}{=} \mathbf{e}_k\mathbf{e}_n\mathbf{e}_n\mathbf{e}_k + \mathbf{e}_k\mathbf{e}_n\mathbf{e}_k\mathbf{e}_n.$$

Here $^4\mathbf{C}$ is macroscopic stiffness tensor; $\mathbf{J}_1$ and $\mathbf{J}_{23}$ are isotropic tensors of the 4th rank; κ, λ and μ are the generalized Lame parameters; $\mathbf{e}_k$ and $\mathbf{e}_n$ are unit vectors of any arbitrary basis.
Macroscopic stiffness tensor is derived in [1] using the expression for the deformation energy of the material

$$W = \frac{1}{2}\varepsilon \cdot\cdot\, ^4\mathbf{C} \cdot\cdot \varepsilon, \qquad ^4\mathbf{C} = {}^4\mathbf{C}^* - {}^3\mathbf{C} \cdot {}^2\mathbf{C}^{-1} \cdot {}^3\mathbf{C}^{\mathsf{T}}, \tag{2}$$

where

$$ {}^4\mathbf{C}^* = \frac{2}{V_0}\left(H_1 \sum_{\alpha=1}^{4} \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha + H_2 \sum_{\alpha,\beta=1}^{4}{}' \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\beta + \right. $$
$$ \left. + H_3 \sum_{\alpha,\beta=1}^{4}{}' (\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\alpha + \mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\alpha\mathbf{n}_\beta) \right), $$

$$ {}^3\mathbf{C} = \frac{1}{V_0} H_4 \sum_{\alpha=1}^{4} \mathbf{n}_\alpha\mathbf{n}_\alpha\mathbf{n}_\alpha, \qquad {}^2\mathbf{C} = \frac{2}{V_0} H_5 \sum_{\alpha=1}^{4} \mathbf{n}_\alpha\mathbf{n}_\alpha, \qquad V_0 = \frac{16\sqrt{3}}{9} a^3. $$

Here W is energy of deformation of the material; ε is strain tensor; ${}^4\mathbf{C}^*$, ${}^3\mathbf{C}$ and ${}^2\mathbf{C}$ are intermediate stiffness tensors; V_0 is volume of an elementary cell of the crystal; a is length of the internuclear bond. The prime at a sum means that summation is conducted on the adjacent bonds only.

Formulae for H_k from [1] in the case of diamond take form:

$$ H_1 = \frac{1}{2} c a^2 - \frac{9}{8} c_\gamma a^2, \qquad H_2 = \frac{1}{8} c_\gamma a^2, \qquad H_3 = \frac{9}{8} c_\gamma a^2, $$
$$ H_4 = c a^2 - 4 c_\gamma a^2, \qquad H_5 = \frac{1}{2} c a^2 + 4 c_\gamma a^2, $$

where $c_\gamma = \dfrac{\gamma}{a^2}$ is the effective stiffness of the angular interaction.
We substitute obtained coefficients H_k and values of vectors $\mathbf{n}_k$ from expression (1) in formulae for intermediate stiffness tensors (4). With the help of the obtained formulae the macroscopic stiffness tensor (3) for diamond can be found. Representing this tensor in form (2) we obtain the following expressions for the generalized Lame parameters:

$$ \kappa = \frac{3\sqrt{3}}{16a} c_\gamma \frac{72 c_\gamma - 7c}{c + 8c_\gamma}, \qquad \lambda = \frac{\sqrt{3}}{12a}(c - 6c_\gamma), \qquad \mu = \frac{3\sqrt{3}}{32a} c_\gamma \frac{15c - 8c_\gamma}{c + 8c_\gamma}. \quad (3) $$

The formulae for elastic constants [3] expressed through generalized Lame parameters take the form:

$$ C_{11} = \kappa + \lambda + 2\mu, \qquad C_{12} = \lambda, \qquad C_{44} = \mu, \qquad K = \frac{\kappa + 3\lambda + 2\mu}{3}, $$
$$ E = \frac{(\kappa + 2\mu)(\kappa + 3\lambda + 2\mu)}{\kappa + 2\lambda + 2\mu}, \qquad \nu = \frac{\lambda}{\kappa + 2\lambda + 2\mu}, \qquad \eta = \frac{2\mu}{\kappa + 2\mu}, $$

where C_{11}, C_{12}, C_{44} are stiffness tensor coefficients; K is the bulk modulus; E is Young modulus; ν is Poisson ratio; η is the anisotropy parameter.
Then by substituting relations for the generalized Lame parameters (6) in the formulae above we obtain:

$$C_{11} = \frac{\sqrt{3}}{12a}(c+12c_\gamma), \qquad C_{12} = \frac{\sqrt{3}}{12a}(c-6c_\gamma), \qquad C_{44} = \frac{3\sqrt{3}}{32a}c_\gamma\frac{15c-8c_\gamma}{c+8c_\gamma} \tag{4}$$

$$K = \frac{\sqrt{3}}{12a}c, \qquad E = \frac{9\sqrt{3}}{4a}\frac{cc_\gamma}{c+3c_\gamma}, \qquad \nu = \frac{1}{2}\frac{c-6c_\gamma}{c+3c_\gamma}, \qquad \eta = \frac{1}{8}\frac{15c-8c_\gamma}{c+8c_\gamma}. \tag{5}$$

2 Comparison with experimental data

Experiment #	1	2	3	4	5
C_{11}, GPa	1079	1076	1076	1100	950
C_{12}, GPa	124	275	125	330	390
C_{44}, GPa	578	519	576	440	430
$\tilde{C}_{44}$, GPa	428	433	427	438	356
error, %	26	16.5	25.9	0.4	17.2
c, N/m	472	578	472	626	615
c_γ, N/m	57	478	56	46	33
c_γ/c, %	12	8.2	12	7.3	5.4

Tab. 1: Experimental and calculated data

In tab. 1 the experimental values for the stiffness tensor components [2] are presented. Such variability of data is caused by various experimental techniques. Coefficients c and c_γ are calculated using the experimental values of C_{11}, C_{12} and formulae (8). Substituting the obtained values in the formula (8) for C_{44} we find the calculated value $\tilde{C}_{44}$. From Tab. 1 it is visible that the maximum divergence of calculated value $\tilde{C}_{44}$ from the experimental data is 26% and minimum is 0.4%. Considering so essential differences in the experimental data the divergence in the obtained values for C_{44} is acceptable. Thus, the given method of calculation gives good coincidence with the experimental values of elastic constants.

3 Comparison with the model based on the moment interaction between atoms

3.1 Moment interaction

The following formulae [3] fulfill:

$$C_{11} = \frac{\sqrt{3}}{12a}(c_A + 2c_D), \qquad C_{12} = \frac{\sqrt{3}}{12a}(c_A - c_D), \qquad C_{44} = \frac{3\sqrt{3}}{8a}\frac{c_A c_D}{c_A + 2c_D},$$

$$K = \frac{\sqrt{3}}{12a}c_A, \qquad G = C_{44} = \frac{3\sqrt{3}}{8a}\frac{c_A c_D}{c_A + 2c_D}, \qquad \nu = \frac{(c_A - c_D)(c_A + 2c_D)}{2c_A^2 + 2c_D^2 + 5c_A c_D},$$

$$^2\mathbf{C} = \frac{4}{3V_0}(c_A + 2c_D)\mathbf{E}, \tag{6}$$

where $^2\mathbf{C}$ is the intermediate stiffness tensor of 2nd rank; c_A and c_D are the longitudinal and transversal stiffness of the bonds.
Condition for the macroscopic stability of a material is the positivity of the bulk modulus K and the shear modulus G

$$K > 0, \qquad G > 0 \qquad \Rightarrow \qquad c_A > 0, \qquad \left| \begin{array}{l} c_D > 0 \\ c_D < -\dfrac{c_A}{2} \end{array} \right. \tag{7}$$

This condition of stability admits negative values for transversal stiffness of the bonds.
A condition for the microscopic stability is the positivity of the coefficient:

$$c_A + 2c_D > 0 \tag{8}$$

From (12) and (13) follows

$$c_A > 0, \qquad c_D > 0. \tag{9}$$

Let us present Poisson ratio as a function of c_D/c_A

$$\nu = \frac{(c_A - c_D)(c_A + 2c_D)}{2c_A^2 + 2c_D^2 + 5c_A c_D} = \frac{1 + \dfrac{c_D}{c_A} - 2\dfrac{c_D^2}{c_A^2}}{2 + 5\dfrac{c_D}{c_A} + 2\dfrac{c_D^2}{c_A^2}} \tag{10}$$

The bounding values for ν are

$c_A \ll c_D \qquad \Rightarrow \qquad \nu \approx -1$

$c_A = c_D \qquad \Rightarrow \qquad \nu = 0 \qquad \Rightarrow \qquad -1 < \nu < \dfrac{1}{2}$

$c_A \gg c_D \qquad \Rightarrow \qquad \nu \approx \dfrac{1}{2}$

From the obtained results it is clear that the model based on the moment atomic interaction gives wide enough area of the admissible values for Poisson ratio, witch include the experimental value [2] $\nu = 0.07$ for diamond.

3.2 Angular interaction

In the first part of this paper the following relations were obtained:

$$C_{11} = \frac{\sqrt{3}}{12a}(c + 12c_\gamma), \qquad C_{12} = \frac{\sqrt{3}}{12a}(c - 6c_\gamma), \qquad C_{44} = \frac{3\sqrt{3}}{32a}c_\gamma\frac{15c - 8c_\gamma}{c + 8c_\gamma},$$

$$K = \frac{\sqrt{3}}{12a}c, \qquad G = C_{44} = \frac{3\sqrt{3}}{32a}c_\gamma\frac{15c - 8c_\gamma}{c + 8c_\gamma}, \qquad \nu = \frac{1}{2}\frac{c - 6c_\gamma}{c + 3c_\gamma},$$

where c is stiffness of the bond, c_γ is the effective stiffness of the angular interaction. If we accept $c_A = c$, $c_D = 6c_\gamma$ then the formulae (10) and (17) for moment and angular interaction will coincide, but only for coefficients C_{11} and C_{12}. However this dose not fulfill for C_{44}.
Using conditions of the macroscopic stability $K > 0, G > 0$ and conditions of the microscopic stability $H_5 > 0$ we obtain the following inequalities

$$c > 0, \qquad 0 < c_\gamma < \frac{15}{8}c. \tag{11}$$

Let us present Poisson ratio as a function of c_γ/c

$$\nu = \frac{1}{2}\frac{c - 6c_\gamma}{c + 3c_\gamma} = \frac{1}{2}\frac{1 - 6\frac{c_\gamma}{c}}{1 + 3\frac{c_\gamma}{c}} \tag{12}$$

The bounding values for ν are

$$c \approx \frac{8}{15}c_\gamma \quad \Rightarrow \quad \nu \approx -\frac{41}{53}$$

$$c = c_\gamma \quad \Rightarrow \quad \nu = -\frac{5}{8} \quad \Rightarrow \quad -\frac{41}{53} < \nu < \frac{1}{2}$$

$$c \gg c_\gamma \quad \Rightarrow \quad \nu \approx \frac{1}{2}$$

Thus, it is visible that the model based on the angular atomic interaction also gives the wide area of the admissible values of Poisson ratio, which covers experimental value. However the lower boundary for Poisson ratio is different for these two models.

4 Conclusion

In the given work the model of diamond using angular atomic interaction was considered. Formulae for the macroscopic stiffness tensor coefficients C_{11}, C_{12}, C_{44}, the bulk modulus K, Young modulus E, Poisson ratio ν, and the anisotropy parameter η in the terms of the stiffness of the bond c and the effective stiffness of angular interaction c_γ were derived. By using the experimental data and the derived formulae the stiffness values of the interatomic bonds c and c_γ were obtained. Comparison with the model based on the moment interaction between atoms was made. It was shown that the considered models give almost identical areas of values for Poisson ratio, and these areas include the experimental value.
This work was supported by the FCNTP and RFBR grant, project 08-01-00865-a.

References

[1] *Krivtsov A.M.* Elastic properties of monoatomic and diatomic crystals.: tutorial. - SPb., Polytechnic University, 2009. - p.124.

[2] *Novikov N.V.* Physical properties of diamond. Handbook. Kiev 1987.

[3] *Berinskiy I.E., Dvas N.G., Krivtsov A.M., Kudarova A.M., Kuzkin V.A., Le-Zakharov A.A., Loboda O.S., Neigebauer I.I., Podolskaya E.A.* Elastic and thermal properties of crystals.: tutorial. - SPb., Polytechnic University, 2009. - p.135.

Sergej Khakalo, Department of Theoretical Mechanics, St. Peterburg State Polytechnical University, Politechnicheskaya, 29, St. Peterburg, 195251, Russia