

Stability analysis of graphite crystal lattice with moment interactions

Igor E. Berinskiy A. M. Krivtsov

`berigor@mail.ru`

Abstract

The main goal of this investigation is to construct and investigate a mathematical model for interaction between carbon atoms in hexagonal graphite lattice. The 2D layer of graphite lattice is considered. The model is based on usage of moment interactions. Carbon atom is simulated by three rigidly bounded material points located at the vertices of an equilateral triangle. The interaction force and moment are determined using a second-rank tensors characterizing stiffness of the summary bond between the triangles. The configuration containing two triangles is considered. Stability of this configuration depending on the distance between triangles and their geometry is investigated. Fourth rank tensors characterizing elastic properties of the lattice are found. Dependence of the lattice stability on the number of the neighboring atoms taken in consideration is investigated.

1 Introduction

It is widely accepted that crystal lattices with a low packing density can not be modelled using pair interactions between the atoms due to instability of such systems. There are two alternative approaches to solve this problem. The first approach is to use many body potentials. But this method meets many difficulties because of too complicated form of potentials. There are also some problems with physical interpretation of the empirical coefficients in these potentials. The second approach is to take into account a moment interaction between atoms. This method is used in the presented paper on the base of a complex mechanical model for a carbon atom. The carbon atom is modelled by three rigidly bounded material points located at the vertices of an equilateral triangle. Every material point of one atom interacts with material points of other atoms using Lennard–Jones potential. Lennard–Jones interaction is used because it has simple physical interpretation and allows preserving the concept of pair interaction between atoms. As a result the summary interaction is not central and consists of two components. First component is a force interaction and is described by force vector. The second one is a moment interaction and is described by moment vector. As it will be shown below the moment component of interaction could give us the additional transversal stiffness to provide the stability of the hexagonal lattice.

This investigation is based on theoretical methods described in [1] for the case of central force interactions. Extension of these methods for moment interactions is presented in [2] for square lattice and [3] for graphite lattice. A mechanical model for carbon nanotube is proposed in [4]. This model uses a set of elastic strings and beams to connect the atoms and provide the system stability. Another way to include rotational degrees of freedom to describe atomic interactions is proposed in works [5] and [6].

The obtained interaction laws can be used in computational experiments based on molecular dynamics method. The results of this investigation could help to obtain a universal form of carbon atoms interaction potential with a possibility of description of different carbon structures.

2 Interactions of non-point particles

Carbon atom is modelled by three rigidly bounded material points located at the vertices of an equilateral triangle. Every material point of one atom interacts with material points of other atoms via Lennard–Jones potential. Let us consider a system of the two equal carbon atoms as it is shown in Fig.1. At the reference configuration distance between atoms is r_0 . The angles between bonds α and β are shown on Fig.1. Let us present internal energy of deformation in the form [2]:

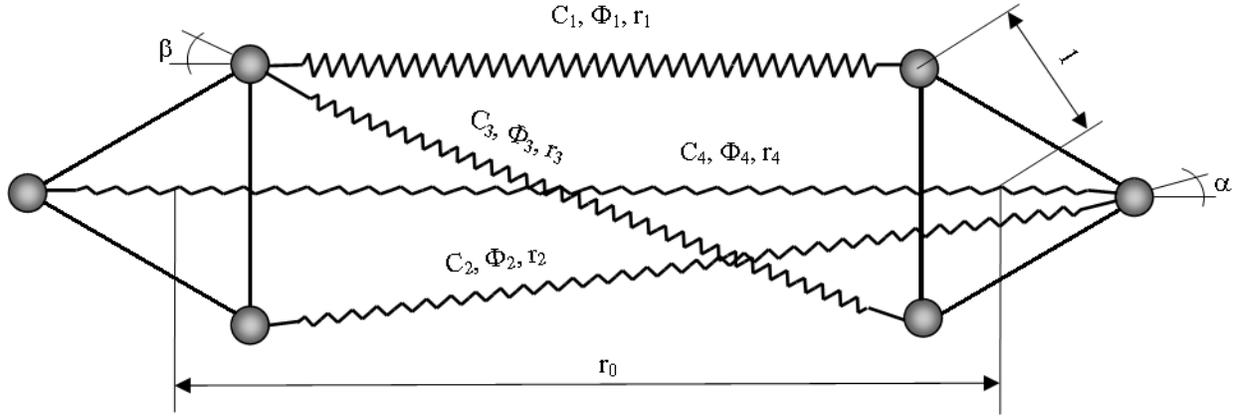


Figure 1: Moment interaction between two particles

$$U = \frac{1}{2} \underline{\varepsilon} \cdot \underline{A} \cdot \underline{\varepsilon} + \underline{\varepsilon} \cdot \underline{B} \cdot \underline{\kappa} + \frac{1}{2} \underline{\kappa} \cdot \underline{C} \cdot \underline{\kappa}. \quad (1)$$

The interaction force and moment are

$$\underline{F} = \underline{A} \cdot \underline{\varepsilon} + \underline{B} \cdot \underline{\kappa}, \quad \underline{M} = \underline{\varepsilon} \cdot \underline{B} + \underline{C} \cdot \underline{\kappa}. \quad (2)$$

Here $\underline{\varepsilon}$ and $\underline{\kappa}$ are deformation vectors:

$$\underline{\varepsilon} = \underline{r} - \underline{r}_0 + \frac{1}{2} \underline{r}_0 \times (\underline{\varphi}_1 + \underline{\varphi}_2), \quad \underline{\kappa} = \underline{\varphi}_2 - \underline{\varphi}_1, \quad (3)$$

where $\underline{r} = \underline{r}_2 - \underline{r}_1$ is a vector that connects the centers of masses of two particles; \underline{r}_0 is a value of \underline{r} at equilibrium position; $\underline{\varphi}_1$ $\underline{\varphi}_2$ are vectors of small rotation of the

particles. Coefficients $\underline{\underline{A}}$, $\underline{\underline{B}}$, and $\underline{\underline{C}}$ are tensors of bonds stiffness. In linear theory stiffness tensors are constant. In general case they are [2]

$$\begin{aligned}\underline{\underline{A}} &= -\sum_{k,n} \underline{\underline{\Psi}}(\xi_{kn}^0), & \underline{\underline{B}} &= \frac{1}{2} \sum_{k,n} \underline{\underline{\Psi}}(\xi_{kn}^0) \times (\rho_k + \rho_n), \\ \underline{\underline{C}} &= \frac{1}{2} \sum_{k,n} \left[\frac{1}{2} r_0 \times \underline{\underline{\Psi}}(\xi_{kn}^0) \times r_0 + \rho_k \times \underline{\underline{\Psi}}(\xi_{kn}^0) \times \rho_n + \rho_n \times \underline{\underline{\Psi}}(\xi_{kn}^0) \times \rho_k \right],\end{aligned}\tag{4}$$

where ξ_{kn}^0 is a difference between absolute radius-vectors of material points that belong to different particles at the reference configuration; ρ_n , ρ_k are radius-vectors of interacting points, they are determined at equilibrium position relatively to centers of the particles. Tensor $\underline{\underline{\Psi}}(\xi)$ is determined on the base of interaction force:

$$\begin{aligned}\underline{\underline{\Psi}}(\xi) &\stackrel{\text{def}}{=} \frac{d}{d\xi} \underline{\underline{f}}(\xi) = 2\Phi'(\xi^2) \xi \xi + \Phi(\xi^2) \underline{\underline{E}} \\ \underline{\underline{f}}(\xi) &= \Phi(\xi^2) \xi_{kn}, & \Phi(\xi^2) &\stackrel{\text{def}}{=} -\frac{1}{\xi_{kn}} \Pi'(\xi_{kn}).\end{aligned}\tag{5}$$

Here Π is some potential (in our case Lennard–Jones potential is used), $\underline{\underline{f}}$ is an interaction force. If the crystal lattice has two orthogonal planes of symmetry then the tensors can be represented in the form:

$$\underline{\underline{A}} = A_{xx} \underline{\underline{i}}\underline{\underline{i}} + A_{yy} \underline{\underline{j}}\underline{\underline{j}}, \quad \underline{\underline{B}} = 0, \quad \underline{\underline{C}} = C_{zz} \underline{\underline{k}}\underline{\underline{k}},\tag{6}$$

Summing all interactions between material points we can find coefficients of the bonds stiffness of triangles:

$$\begin{aligned}A_{xx} &= 2C_1 + C_4 + 4C_2 \cos^2 \alpha + 2C_3 \cos^2 \beta - (4\Phi_2 \sin^2 \alpha + 2\Phi_3 \sin^2 \beta) \\ A_{yy} &= 4C_2 \sin^2 \alpha + 2C_3 \sin^2 \beta - (2\Phi_1 + \Phi_4 + 4\Phi_2 \cos^2 \alpha + 2\Phi_3 \cos^2 \beta), \\ C_{zz} &= \frac{1}{4} A_{yy} r_0^2 + (C_1 - C_4 + 2C_2 - 2C_3) l^2 + \frac{1}{2} l^2 (C_1 + \Phi_1) + l^2 (C_4 + \Phi_4), \\ &+ (C_3 + \Phi_3) l^2 (\cos \beta - \sqrt{3} \sin \beta)^2 - 2l^2 (C_2 + \Phi_2) \cos^2 \alpha.\end{aligned}\tag{7}$$

Here $C_i \stackrel{\text{def}}{=} -f'(\xi)_i$ are the stiffnesses between different points, C_i and Φ_i are shown in Fig. 1.

3 Stability of the system of two-particles configuration

Let us investigate stability of the system considered above using Lennard – Jones potential for description of interaction between points:

$$\Pi(r) = D \left(\left(\frac{\rho}{r} \right)^{12} - 2 \left(\frac{\rho}{r} \right)^6 \right).\tag{8}$$

Then the stiffness for $i = 1, 2, 3, 4$ is

$$C_i = \Pi''(r)|_{r=r_i}.\tag{9}$$

Let us use two new variables

$$\zeta = \frac{l}{r_0}, \quad \eta = \frac{\rho}{r_0}, \quad (10)$$

where l is an effective size of the particle — a typical dimension, which is equal to distance from the centre of the “triangle” to it’s vertices. Using geometry of the model we obtain:

$$\begin{aligned} r_1 &= r_0(1 - \zeta), & r_2 &= r_0\sqrt{1 + \zeta + \zeta^2}, \\ r_3 &= r_0\sqrt{(1 - \zeta)^2 + 3\zeta^2}, & r_4 &= r_0(1 + 2\zeta). \end{aligned} \quad (11)$$

Now we can write for every stiffness:

$$C_i = \frac{D}{\rho^2} \gamma_i(\eta, \zeta), \quad i = 1..4, \quad (12)$$

where γ_i is dimensionless algebraic function of η and ζ . For every particle we obtain the force balance equation

$$2f(r_1) + 4f(r_2) \cos \alpha + 2f(r_3) \cos \beta + f(r_4) = 0. \quad (13)$$

Here $f = -\Pi'(r)$ is the force of interaction. Equation (13) gives us relation between the variables

$$\eta^6 = \frac{\frac{1}{(1 - \zeta)^7} + \frac{2 + \zeta}{(1 + \zeta + \zeta^2)^4} + \frac{1 - \zeta}{((1 - \zeta)^2 + 3\zeta^2)^4} + \frac{1}{2(1 + 2\zeta)^7}}{\frac{1}{(1 - \zeta)^{13}} + \frac{2 + \zeta}{(1 + \zeta + \zeta^2)^7} + \frac{1 - \zeta}{((1 - \zeta)^2 + 3\zeta^2)^7} + \frac{1}{2(1 + 2\zeta)^{13}}} \quad (14)$$

It is possible to provide stability of the sistem only if the quadratic form (1) is positively defined. This condition is provided by applying the inequalities

$$A_{xx} > 0, \quad A_{yy} > 0, \quad C_{zz} > 0. \quad (15)$$

Using (7) we can obtain a system of inequalities in terms of ζ and η . Using (14) gives the conditions for ζ . Numerical analysis only shows that system (15) is reduced to one inequality $A_{yy} > 0$, which can be represented as a stability condition for two-particles system:

$$\zeta < 0.230 \Leftrightarrow l < 0.230r_0. \quad (16)$$

Thus ζ has the upper bond. That means that triangle size is limited in comparison with the distance between the centers of triangles.

4 Stability of the hexagonal plane lattice

The total system of equations of macroscopic moment theory of elasticity can be wrutten in the form [3]:

$$\begin{aligned} \nabla \cdot \underline{\underline{\tau}} + \underline{\underline{f}} &= \rho \underline{\underline{\ddot{u}}}, & \nabla \cdot \underline{\underline{\mu}} + \underline{\underline{\tau}}_{\times} + \underline{\underline{m}} &= \rho \underline{\underline{\vartheta}} \cdot \underline{\underline{\ddot{\varphi}}}, \\ \underline{\underline{\tau}} &= {}^4\underline{\underline{A}} \cdot \underline{\underline{\varepsilon}}, & \underline{\underline{\mu}} &= {}^4\underline{\underline{C}} \cdot \underline{\underline{\kappa}}, \\ \underline{\underline{\varepsilon}} &= \nabla \underline{\underline{u}} + \underline{\underline{E}} \times \underline{\underline{\varphi}}, & \underline{\underline{\kappa}} &= \nabla \underline{\underline{\varphi}}. \end{aligned} \quad (17)$$

Here ρ is the mass density, $\underline{\underline{J}}$ is a tensor of inertia per unit of mass, \underline{f} is a volume density of external forces and \underline{m} is a volume density of external moments.

The considered 2D lattice has space symmetry of the 3rd order, therefore the tensor of stiffness ${}^4\underline{\underline{A}}$ is isotropic and can be represented in the form:

$${}^4\underline{\underline{A}} = A_1\underline{\underline{J}}_1 + A_2\underline{\underline{J}}_2 + A_3\underline{\underline{J}}_3, \quad (18)$$

where tensors $\underline{\underline{J}}_k$ are

$$\underline{\underline{J}}_1 = e_k e_k e_n e_n, \quad \underline{\underline{J}}_2 = e_k e_n e_n e_k, \quad \underline{\underline{J}}_3 = e_k e_n e_k e_n. \quad (19)$$

For the graphite lattice in the nearest neighbors approximation (Fig.2) the coefficients A_k have the form [3]

$$\begin{aligned} A_1 &= \frac{\sqrt{3}}{12} r_0^2 \left(A - D + \frac{(A - D)^2}{A + D} \right), \\ A_2 &= \frac{\sqrt{3}}{12} r_0^2 \left(A + 3D - \frac{(A - D)^2}{A + D} \right), \\ A_3 &= \frac{\sqrt{3}}{12} r_0^2 \left(A - D - \frac{(A - D)^2}{A + D} \right), \end{aligned} \quad (20)$$

where stiffness coefficients A and D can be represented in the terms of the bonds stiffness of triangle particles by following relations

$$A_{xx} = Ar_0^2, \quad A_{yy} = Dr_0^2. \quad (21)$$

Moment tensor of stiffness is

$${}^4\underline{\underline{C}} = \sqrt{3} C (i\underline{k}\underline{k}i + j\underline{k}\underline{k}j), \quad (22)$$

where C is a torsion stiffness:

$$C_{zz} = C. \quad (23)$$

Here the distance between the nearest neighbors in the lattice differs from the Lennard–Jones equilibrium distance because of using the complex particles instead of materials points. If the nearest neighbors are considered only then the equilibrium equation leads to formula (13) and the distance between the nearest atoms in the lattice becomes equal to the distance between centers of the triangles. That is why the consideration of two interacting triangle particles was essential to find relations between size of particles and the distance between them. Now let us obtain the general stability conditions for the lattice.

Let us use expression for the density of internal deformation energy as a quadratic form of deformation tensors [3]:

$$\rho U = \frac{1}{2} \underline{\underline{\varepsilon}}^T \cdot \cdot {}^4\underline{\underline{A}} \cdot \cdot \underline{\underline{\varepsilon}} + \frac{1}{2} \underline{\underline{\kappa}}^T \cdot \cdot {}^4\underline{\underline{C}} \cdot \cdot \underline{\underline{\kappa}}, \quad (24)$$

where components of the stiffness tensors could be found from (20) and (22). The criterion of stability of the material is a positive definiteness of quadratic form (24). Every term in the form is independent so we can obtain two independent conditions:

$$\underline{\underline{\varepsilon}}^T \cdot \cdot {}^4\underline{\underline{A}} \cdot \cdot \underline{\underline{\varepsilon}} > 0, \quad \underline{\underline{\kappa}}^T \cdot \cdot {}^4\underline{\underline{C}} \cdot \cdot \underline{\underline{\kappa}} > 0. \quad (25)$$

The deformation tensors have the form:

$$\begin{aligned}\underline{\underline{\varepsilon}} &= \varepsilon_{xx}\underline{i}\underline{i} + \varepsilon_{xy}\underline{i}\underline{j} + \varepsilon_{yx}\underline{j}\underline{i} + \varepsilon_{yy}\underline{j}\underline{j}, \\ \underline{\underline{\kappa}} &= \kappa_{xz}\underline{i}\underline{k} + \kappa_{yz}\underline{j}\underline{k}.\end{aligned}\tag{26}$$

Substitution of the first formula from (26) to (25) leads to inequality

$$A_1(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + 2\varepsilon_{xx}\varepsilon_{yy}) + A_2(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{xy}^2 + \varepsilon_{yx}^2) + A_3(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + 2\varepsilon_{xy}\varepsilon_{yx}) > 0, \tag{27}$$

where A_1, A_2, A_3 are presented in (20). It gives us four independent conditions:

$$\begin{aligned}A_2 > 0, \quad A_2^2 - A_3^2 > 0, \quad A_1 + A_2 + A_3 > 0, \\ (A_1 + A_2 + A_3)^2 - A_1^2 > 0.\end{aligned}\tag{28}$$

Let us suppose that the longitudinal stiffness A and transverse stiffness D are positive. Then the four inequalities (28) can be reduced to the following conditions:

$$A > D, \quad D > 0.\tag{29}$$

Numerical analysis shows that the first inequality always fulfills in the terms of ζ . Therefore the essential condition is the second one. At the same time it leads to just found inequality for transverse bonds stiffness of triangles $A_{yy} > 0$. It means coincidence of results on microlevel and macrolevel.

Let us take the second formula from (26) and substitute it to (25). It leads to the condition

$$C(\kappa_{xz}^2 + \kappa_{yz}^2) > 0,\tag{30}$$

which fulfills for every positive C .

5 Second-order neighbors consideration

The equilibrium condition obtained above coincide with (15) and gives us upper bound of the particle size versus distance between the particles. But the lower value is equal to zero. It means that it is possible to use infinitely small triangles e.g. material points. But it is well known that using material points as the models of particles usually can not provide lattice stability. The reason is that second-order and further neighbours are located at the distance that corresponds to the unstable part of the Lennard-Jones force–distance diagram where bond stiffness values are negative. That means that taking into account nearest neighbors only is not sufficient because of significant influence of the far neighbours on the system stability. Let us consider the atoms that belong to the second coordination sphere. They are at distance $b = \sqrt{3}r_0$ from the given atom (Fig.2). Let us neglect the shear stiffness for the next neighbors. That means that the interaction between the far neighbors is the interaction between the material points. Force balance equation is

$$\tilde{f}_1(r_0) + 2\sqrt{3}\tilde{f}_2(\sqrt{3}r_0) = 0,\tag{31}$$

where $\tilde{f}_1(r_0)$ is a sum of all the interactions on the first coordination sphere. It coincides with the left part of the equation (13) so long as $r = r_0$. The $\tilde{f}_2(\sqrt{3}r_0)$

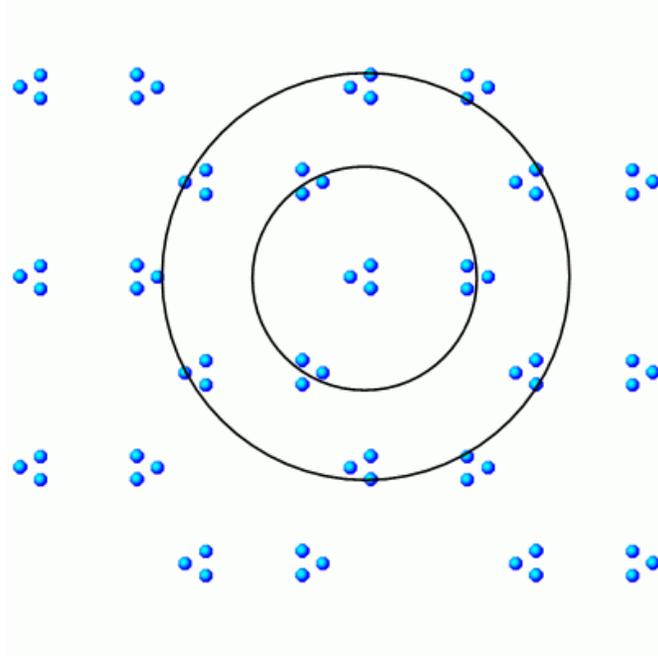


Figure 2: First and second-order neighbors in the lattice

term corresponds for the next neighbors interaction. Solution of equation (31) gives in our case the relation analogical to (14):

$$\eta^6 = \frac{\frac{1}{3^3} + \frac{1}{(1-\zeta)^7} + \frac{2+\zeta}{(1+\zeta+\zeta^2)^4} + \frac{1-\zeta}{((1-\zeta)^2+3\zeta^2)^4} + \frac{1}{2(1+2\zeta)^7}}{\frac{1}{3^6} + \frac{1}{(1-\zeta)^{13}} + \frac{2+\zeta}{(1+\zeta+\zeta^2)^7} + \frac{1-\zeta}{((1-\zeta)^2+3\zeta^2)^7} + \frac{1}{2(1+2\zeta)^{13}}} \quad (32)$$

Using [3] approximation, where coefficients A_k for nearest neighbors are found in, let us find stiffness tensors for our case:

$$\begin{aligned} A_1 &= \frac{\sqrt{3}}{12} r_0^2 \left(A - D + 18B + \frac{(A-D)^2}{A+D+6B} \right), \\ A_2 &= \frac{\sqrt{3}}{12} r_0^2 \left(A + 3D + 18B - \frac{(A-D)^2}{A+D+6B} \right), \\ A_3 &= \frac{\sqrt{3}}{12} r_0^2 \left(A - D + 18B - \frac{(A-D)^2}{A+D+6B} \right), \end{aligned} \quad (33)$$

where $B < 0$ is a stiffness coefficient for second neighbours bonds. Now we can use (32) to obtain the stability conditions as it was done for the nearest neighbours approximation. Numeric solution of inequalities (28) for ζ gives in case of Lennard–Jones potential the following relation between the size of triangles l and the distance r_0 between centers of them

$$0.082r_0 < l < 0.224r_0. \quad (34)$$

Thus taking into account the second neighbours allows obtaining the lower bound in addition to the more accurate upper value.

6 Conclusions

This work presents a mechanical model which can describe 2D graphite crystal lattice. It is shown that moment interactions can provide the lattice stability. It is shown that stability depends on the parameter that is ratio between the effective size of the atom and the distance between the centers of the neighboring atoms. The lower and upper bounds of the stability area for this parameter are investigated. The upper bound is connected with stability of the summary interaction. The lower bound characterizes balance between stabilizing moment interaction between the first-order neighbors and destabilizing force interaction between the second-order neighbors. This balance became essential for the small effective sizes of the atom. It is possible to find all necessary parameters of interaction choosing the effective size of the atom within the stability area.

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Igor E. Berinskiy, Anton M. Krivtsov. Institute for Problems in Mechanical Engineering Russian Academy of Sciences, Bolshoy pr. V. O., 61, St. Petersburg, 199178, Russia.