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FORCE CONSTANT MATRICES FROM KEATING INTERATOMIC POTENTIAL: APPLICATION TO GRAPHENE

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Based on the Keating interatomic potential an analytical derivation of force constant matrices of two- and three-body interactions in crystals is performed. Using the derived force constant matrices the in-plane phonon energy spectra of graphene was calculated in the framework of a lattice dynamics theory. A reasonable agreement with experimental data was obtained. The results can extend the applicability of the current force constant models for investigation of crystal dynamics.

Keywords: *force constant matrices, Keating potential, graphene, phonons, crystal dynamics*.

MATRICELE CONSTANTELOR DE FORŢĂ DIN POTENŢIALUL INTERATOMAR AL LUI KEATING: APLICAREA CĂTRE GRAFEN

În baza potenţialului interatomar al lui Keating au fost deduse analitic matricele constantelor de forţă ale interacţiunilor a două şi trei particule în cristale. Utilizând aceste matrice, în cadrul teoriei dinamicii reţelei cristaline a fost calculat spectrul fononic al grafenului în planul stratului. A fost obţinut un acord rezonabil cu datele experimentale. Aceste rezultate pot extinde aplicabilitatea modelelor constantelor de forţă curente la studierea dinamicii cristalelor.

Cuvinte-cheie: *matricele constantelor de forţă, potenţialul lui Keating, grafen, fononi, dinamica cristalelor*.

Introduction

Modeling of different properties of crystals and crystalline nanostructures is accomplished either on the atomic level, by lattice dynamics (LD) or molecular dynamics (MD) methods, or on the electronic structure level, using ab initio techniques such as density functional theory. One of the main advantages of lattice dynamics is that, in contrast to molecular dynamics or ab initio simulations, it does not require large computational times.

The major part of LD models are based on the empirical force constant matrices [1-3] and thus, are strongly limited in predicting the properties of materials with a lack of experimental data on phonon frequencies in high-symmetry points of Brillouin zone. MD methods, which are based on the empirical interatomic potentials [4-6], have a wider applicability, since the parameters of interatomic potentials can be fitted on a different set of experimental data. However, it is possible to derive the force constant matrices from interatomic potentials and thus to extend the applicability of conventional LD models. In this work the problem of obtaining analytic expressions for force constant matrices including contributions of two- and three-body interaction potentials is solved in the harmonic approximation.

Theory

Let us introduce the following notations: N – number of atoms in unit cell, N_{sph} – number of neighbour atomic spheres, $n_s(i)$ – number of atoms on the s-th neighbour sphere of atom i, $\vec{u}_i$ – vector of displacement of i-th atom from the i-th lattice node, $\vec{r}_i$ – radius-vector of i-th lattice node (equilibrium position of i-th atom), $\vec{R}_i$ – radius-vector of i-th atom.

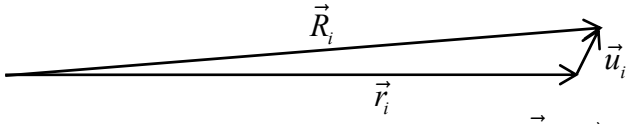

Fig.1. Vector scheme. The vectors are related as: $\vec{R}_i = \vec{r}_i + \vec{u}_i$.

Consider the total potential energy of the crystal lattice as a sum of two-body "stretching" and three-body "bending" potentials:

$$V = V^{str} + V^{bend}. \quad (1)$$

In general case, in potential (1) are involved all atoms of the crystal. However, since the crystal possesses periodicity and since the interatomic interaction usually has a short-range action, it is convenient to limit the consideration only to a few neighbour atomic spheres. In this case, V can be rewritten as follows:

$$V = \sum_{s=1}^{N_{sph}} \left(V_s^{str} + V_s^{bend} \right). \tag{2}$$

In case of the Keating potential the two- and three-body terms in equation (2) are determined by the following expressions:

$$V_s^{str} = \frac{1}{2} \kappa_s^{str} \sum_{i=1}^{N} \sum_{j=1}^{n_s(i)} (\delta r_{ij})^2 , \tag{3}$$

where κ_s^{str} - force constant of two-body stretching interaction between atoms from s-th sphere, δr_{ij} - small deviation of the i-j bond from equilibrium, and:

$$V_s^{bend} = \frac{1}{2} d_s^2 \kappa_s^{bend} \sum_{i=1}^{N} \sum_{j=1}^{n_s(i)} \sum_{k \neq j}^{n_s(i)} (\delta \theta_{jik})^2 , \tag{4}$$

where κ_s^{bend} - force constant of three-body bending interaction between atoms from s-th sphere, $\delta \theta_{jik}$ - small bending of the j-i-k bond from equilibrium, d_s - radius of the s-th neighbour sphere.

P. Keating noted [3], that the total potential energy of the interatomic interaction should be invariant under an arbitrary (i) displacement and (ii) rotation of the crystal lattice as a whole. The first condition (displacement invariance) ensures that V can depend only on the differences between atomic positions $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$. The second condition (rotation invariance) is satisfied only if V is formed from the scalar products between $\vec{r}_{ij}$ e.g. $\vec{r}_{ij}\vec{r}_{kl}$, $\vec{r}_{ij}\vec{r}_{ik}$, $\vec{r}_{ij}\vec{r}_{ij}$, etc.

In the harmonic approximation, the potential energy can be written as:

$$V = -\frac{1}{2} \sum_{\alpha,\beta=x,y,z} \sum_{s=1}^{N_{sph}} \sum_{i=1}^{N} \sum_{j=1}^{n_s(i)} \left(\Phi_{\alpha\beta}^{str,s}(i,j) + \Phi_{\alpha\beta}^{bend,s}(i,j) \right) u_{ij,\alpha} u_{ij,\beta} . \tag{5}$$

The elements of the force constant matrices are second derivatives from corresponding potential energies on atomic displacements, taken at equilibrium positions. In case of stretching interaction:

$$\Phi_{\alpha\beta}^{str,s}(i,j) = \frac{\partial^2 V_s^{str}}{\partial u_{i,\alpha} \partial u_{j,\beta}} \tag{6}$$

In case of bending interactions:

$$\Phi_{\alpha\beta}^{bend,s}(i,j) = \frac{\partial^2 V_s^{bend}}{\partial u_{i,\alpha} \partial u_{j,\beta}} \tag{7}$$

Equation (7) describes an indirect interaction between atoms i and j through a third atom. In order to calculate the force constant matrices from equations (6-7) one should express the stretching deviation δr_{ij} and angle deviation $\delta \theta_{jik}$ in terms of radius-vectors of the lattice nodes r_{ij} and displacements u_{ij}. Below is presented a detailed analytical derivation of the force constant matrices of two- and three-body interactions.

Two-body "stretching" interaction

The stretching deviation δr_{ij} can be defined as:

$$\delta r_{ij} = R_{ij} - r_{ij} . \tag{8}$$

At the same time, the distance between atoms i and j, i.e. R_{ij} can be expressed through atomic displacements u_{ij} as:

$$\begin{aligned} R_{ij} &= \sqrt{\sum_{\gamma=x,y,z} (r_{ij,\gamma} + u_{ij,\gamma})^2} = \sqrt{\sum_{\gamma=x,y,z} (r_{ij,\gamma})^2 + \sum_{\gamma=x,y,z} 2 r_{ij,\gamma} u_{ij,\gamma} + \sum_{\gamma=x,y,z} (u_{ij,\gamma})^2} \approx \\ &\approx \sqrt{\sum_{\gamma=x,y,z} (r_{ij,\gamma})^2 + \sum_{\gamma=x,y,z} 2 r_{ij,\gamma} u_{ij,\gamma}} = \sqrt{(\vec{r}_{ij})^2 + 2\vec{r}_{ij}\vec{u}_{ij}} = r_{ij} \sqrt{1 + 2\frac{\vec{r}_{ij}\vec{u}_{ij}}{(\vec{r}_{ij})^2}} \approx r_{ij} \left(1 + \frac{\vec{r}_{ij}\vec{u}_{ij}}{(\vec{r}_{ij})^2} \right) = r_{ij} + \frac{\vec{r}_{ij}\vec{u}_{ij}}{r_{ij}} . \end{aligned} \tag{9}$$

Introducing equation (9) into (8) one can obtain for deviation δr_{ij} a simple expression:

$$\delta r_{ij} = \frac{\vec{r}_{ij}\vec{u}_{ij}}{r_{ij}} \tag{10}$$

Using this relation the two-body "stretching" potential can be written as:

$$V_s^{str} = \frac{1}{2}\kappa_s^{str}\sum_{i=1}^{N}\sum_{j=1}^{n_s(i)}\left(\frac{\vec{r}_{ij}\vec{u}_{ij}}{r_{ij}}\right)^2 = \frac{1}{2}\frac{\kappa_s^{str}}{d_s^2}\sum_{i=1}^{N}\sum_{j=1}^{n_s(i)}(\vec{r}_{ij}\vec{u}_{ij})^2 \tag{11}$$

Note, that potential (11) satisfies the displacement and rotation invariance conditions, since it is expressed only through a scalar products $\vec{r}_{ij}\vec{u}_{ij}$. Force constant matrices of two-body interactions are calculated from formula (6) as:

$$\Phi_{\alpha\beta}^{str,s}(i,j) = \frac{\partial^2 V_s^{str}}{\partial u_{i,\alpha}\partial u_{j,\beta}} = \frac{\partial}{\partial u_{i,\alpha}}\left(\frac{\partial}{\partial u_{j,\beta}}\left(\frac{1}{2}\frac{\kappa_s^{str}}{d_s^2}\sum_{i=1}^{N}\sum_{j=1}^{n_s(i)}(\vec{r}_{ij}\vec{u}_{ij})^2\right)\right) =$$

$$= \frac{\kappa_s^{str}}{d_s^2}\frac{\partial}{\partial u_{i,\alpha}}\left(\sum_{i=1}^{N}(\vec{r}_{ij}\vec{u}_{ij})\times\frac{\partial}{\partial u_{j,\beta}}\left(\sum_{j=1}^{n_s(i)}\vec{r}_{ij}\vec{u}_{ij}\right)\right) = \frac{\kappa_s^{str}}{d_s^2}\frac{\partial}{\partial u_{i,\alpha}}\left(\sum_{i=1}^{N}\left((\vec{r}_{ij}\vec{u}_{ij})\times r_{ij,\beta}\right)\right) = ,$$

$$= \frac{\kappa_s^{str}}{d_s^2}r_{ij,\beta}\frac{\partial}{\partial u_{i,\alpha}}\left(\vec{r}_{ij}\vec{u}_{ij}\right) = -\frac{\kappa_s^{str}}{d_s^2}r_{ij,\alpha}r_{ij,\beta}$$

thus:

$$\Phi_{\alpha\beta}^{str,s}(i,j) = -\frac{\kappa_s^{str}}{d_s^2}r_{ij,\alpha}r_{ij,\beta}\,. \tag{12}$$

Three-body "bending" interaction

The angle deviation $\delta\theta_{jik}$ can be defined as:

$$\delta\theta_{jik} = \theta_{jik} - \theta_{jik}^0\,. \tag{13}$$

The cosine of the angle θ_{jik} can be expressed through displacements u_{ij} using the definition of the scalar product $\vec{R}_{ij}\vec{R}_{ik}$:

$$\cos\theta_{jik} = \frac{\vec{R}_{ij}\vec{R}_{ik}}{\left|\vec{R}_{ij}\right|\left|\vec{R}_{ik}\right|} = \frac{\left(\vec{r}_{ij}+\vec{u}_{ij}\right)\left(\vec{r}_{ik}+\vec{u}_{ik}\right)}{\left|\vec{r}_{ij}+\vec{u}_{ij}\right|\left|\vec{r}_{ik}+\vec{u}_{ik}\right|} = \frac{\vec{r}_{ij}\vec{r}_{ik}+\vec{r}_{ij}\vec{u}_{ik}+\vec{r}_{ik}\vec{u}_{ij}+\vec{u}_{ij}\vec{u}_{ik}}{\sqrt{(\vec{r}_{ij})^2+2\vec{r}_{ij}\vec{u}_{ij}+(\vec{u}_{ij})^2}\sqrt{(\vec{r}_{ik})^2+2\vec{r}_{ik}\vec{u}_{ik}+(\vec{u}_{ik})^2}} \approx$$

$$\approx \frac{\vec{r}_{ij}\vec{r}_{ik}+\vec{r}_{ij}\vec{u}_{ik}+\vec{r}_{ik}\vec{u}_{ij}}{\sqrt{(\vec{r}_{ij})^2+2\vec{r}_{ij}\vec{u}_{ij}}\sqrt{(\vec{r}_{ik})^2+2\vec{r}_{ik}\vec{u}_{ik}}} \approx \frac{\vec{r}_{ij}\vec{r}_{ik}+\vec{r}_{ij}\vec{u}_{ik}+\vec{r}_{ik}\vec{u}_{ij}}{r_{ij}r_{ik}\sqrt{1+2\frac{\vec{r}_{ij}\vec{u}_{ij}}{r_{ij}^2}}\sqrt{1+2\frac{\vec{r}_{ik}\vec{u}_{ik}}{r_{ik}^2}}} \approx \frac{\vec{r}_{ij}\vec{r}_{ik}+\vec{r}_{ij}\vec{u}_{ik}+\vec{r}_{ik}\vec{u}_{ij}}{r_{ij}r_{ik}\left(1+\frac{\vec{r}_{ij}\vec{u}_{ij}}{r_{ij}^2}\right)\left(1+\frac{\vec{r}_{ik}\vec{u}_{ik}}{r_{ik}^2}\right)} = . \tag{14}$$

$$= \frac{\vec{r}_{ij}\vec{r}_{ik}+\vec{r}_{ij}\vec{u}_{ik}+\vec{r}_{ik}\vec{u}_{ij}}{r_{ij}r_{ik}+\frac{r_{ij}}{r_{ik}}\vec{r}_{ik}\vec{u}_{ik}+\frac{r_{ik}}{r_{ij}}\vec{r}_{ij}\vec{u}_{ij}+\frac{\vec{r}_{ij}\vec{u}_{ij}\vec{r}_{ik}\vec{u}_{ik}}{r_{ij}r_{ik}}} \approx \frac{\vec{r}_{ij}\vec{r}_{ik}+\vec{r}_{ij}\vec{u}_{ik}+\vec{r}_{ik}\vec{u}_{ij}}{r_{ij}r_{ik}+\frac{r_{ij}}{r_{ik}}\vec{r}_{ik}\vec{u}_{ik}+\frac{r_{ik}}{r_{ij}}\vec{r}_{ij}\vec{u}_{ij}}$$

In equilibrium configuration the following relations are true: $r_{ij} = r_{ik} = d_s$, $\cos\theta_{jik}^0 = \frac{\vec{r}_{ij}\vec{r}_{ik}}{d_s^2}$, where d_s is the radius of *s*-th atomic sphere. Therefore equation (14) can be rewritten as:

$$\cos\theta_{jik}=\frac{d_s^2\cos\theta_{jik}^0+\vec{r}_{ij}\vec{u}_{ik}+\vec{r}_{ik}\vec{u}_{ij}}{d_s^2+\vec{r}_{ii}\vec{u}_{ik}+\vec{r}_{ij}\vec{u}_{ij}}=\left(\cos\theta_{jik}^0+\frac{\vec{r}_{ij}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ik}\vec{u}_{ij}}{d_s^2}\right)\frac{1}{1+\frac{\vec{r}_{ik}\vec{u}_{ik}+\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}}\approx$$

$$\approx\left(\cos\theta_{jik}^0+\frac{\vec{r}_{ij}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ik}\vec{u}_{ij}}{d_s^2}\right)\left(1-\frac{\vec{r}_{ik}\vec{u}_{ik}+\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}\right)=\cos\theta_{jik}^0\left(1-\frac{\vec{r}_{ik}\vec{u}_{ik}+\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}\right)+\frac{\vec{r}_{ij}\vec{u}_{ik}}{d_s^2}\left(1-\frac{\vec{r}_{ik}\vec{u}_{ik}+\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}\right)+. \quad (15)$$

$$+\frac{\vec{r}_{ik}\vec{u}_{ij}}{d_s^2}\left(1-\frac{\vec{r}_{ik}\vec{u}_{ik}+\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}\right)\approx\cos\theta_{jik}^0-\cos\theta_{jik}^0\frac{\vec{r}_{ik}\vec{u}_{ik}}{d_s^2}-\cos\theta_{jik}^0\frac{\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}+\frac{\vec{r}_{ij}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ik}\vec{u}_{ij}}{d_s^2}$$

It is possible to express the angle deviation $\delta\theta_{jik}$ through $\cos\theta_{jik}$:

$$\cos\theta_{jik}-\cos\theta_{jik}^0=\cos\left(\theta_{jik}^0+\delta\theta_{jik}\right)-\cos\theta_{jik}^0=\cos\theta_{jik}^0\cos\left(\delta\theta_{jik}\right)-$$
$$-\sin\theta_{jik}^0\sin\left(\delta\theta_{jik}\right)-\cos\theta_{jik}^0\approx-\sin\theta_{jik}^0\delta\theta_{jik}$$

thus:

$$\delta\theta_{jik}=-\frac{1}{\sin\theta_{jik}^0}\left(\cos\theta_{jik}-\cos\theta_{jik}^0\right). \quad (16)$$

Introducing (15) into (16):

$$\delta\theta_{jik}=-\frac{1}{\sin\left(\theta_{jik}^0\right)}\left(\cos\left(\theta_{jik}\right)-\cos\left(\theta_{jik}^0\right)\right)=\mathrm{ctg}\left(\theta_{jik}^0\right)\left(\frac{\vec{r}_{ik}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}\right)-\frac{1}{\sin\left(\theta_{jik}^0\right)}\left(\frac{\vec{r}_{ij}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ik}\vec{u}_{ij}}{d_s^2}\right). \quad (16)$$

Using this relation the three-body "bending" potential can be written as:

$$V_s^{bend}=\frac{1}{2}d_s^2\kappa_s^{bend}\sum_{i=1}^{N}\sum_{j=1}^{n_s(i)}\sum_{k\neq j}^{n_s(i)}\left(\mathrm{ctg}\theta_{jik}^0\left(\frac{\vec{r}_{ik}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}\right)-\frac{1}{\sin\theta_{jik}^0}\left(\frac{\vec{r}_{ij}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ik}\vec{u}_{ij}}{d_s^2}\right)\right)^2. \quad (17)$$

Potential (17) is expressed through simple scalar products $\vec{r}_{ik}\vec{u}_{ik}$, $\vec{r}_{ij}\vec{u}_{ij}$, $\vec{r}_{ij}\vec{u}_{ik}$, $\vec{r}_{ik}\vec{u}_{ij}$ and therefore it satisfies the conditions imposed by displacement and rotational invariance. Force constant matrices of three-body interactions are calculated from equation (7) as:

$$\Phi_{\alpha\beta}^{bend,s}(i,j)=\frac{\partial^2V_s^{bend}}{\partial u_{i,\alpha}\partial u_{j,\beta}}=\frac{1}{2}d_s^2\kappa_s^{bend}\frac{\partial}{\partial u_{i,\alpha}}\left(\frac{\partial}{\partial u_{j,\beta}}\left(\sum_{i=1}^{N}\sum_{j=1}^{n_s(i)}\sum_{k\neq j}^{n_s(i)}\left(\mathrm{ctg}\theta_{jik}^0\left(\frac{\vec{r}_{ik}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ij}\vec{u}_{ij}}{d_s^2}\right)-\right.\right.\right.$$
$$\left.\left.\left.-\frac{1}{\sin\theta_{jik}^0}\left(\frac{\vec{r}_{ij}\vec{u}_{ik}}{d_s^2}+\frac{\vec{r}_{ik}\vec{u}_{ij}}{d_s^2}\right)\right)^2\right)\right). \quad (18)$$

After the derivation over $u_{i,\alpha}$ and $u_{j,\beta}$ one can obtain for $\Phi_{\alpha\beta}^{bend,s}$:

$$\Phi_{\alpha\beta}^{bend,s}(i,j)=2\frac{\kappa_s^{bend}}{d_s^2}\sum_{k\neq j}^{n_s(i)}\left(\frac{1-\cos\theta_{jik}^0}{\sin^2\theta_{jik}^0}\left(r_{ij,\alpha}\cos\theta_{jik}^0-r_{ik,\alpha}\right)\left(r_{ij,\beta}+r_{ik,\beta}\right)\right). \quad (19)$$

Application to graphene

Using the force constant matrices of two-body interactions defined by equation (12) and of three-body interactions defined by equation (19), one can calculate the phonon dispersion of a crystal within the Born – von Karman lattice dynamics theory [2]. In this work I will consider the case of a novel 2D material – graphene – an atomic layer of carbon atoms arranged in a honeycomb lattice. Graphene has hexagonal crystal symmetry with 2 atoms in primitive unit cell (denoted below as '1' and '2'). On the first atomic sphere of atom *i*=1 there are 3 atoms with coordinates: $\vec{r}_{11}=(a,0)$, $\vec{r}_{12}=(-\frac{a}{2},-\frac{a\sqrt{3}}{2})$, $\vec{r}_{13}=(-\frac{a}{2},\frac{a\sqrt{3}}{2})$, where *a*=0.142 nm is carbon-carbon bond length.

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Force constant matrices of two-body interaction from equation (12) are: $\Phi^{str}(1,1) = -\kappa^{str}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$,

$\Phi^{str}(1,2) = -\kappa^{str}\begin{pmatrix} 1/4 & \sqrt{3}/4 & 0 \\ \sqrt{3}/4 & 3 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ and $\Phi^{str}(1,3) = -\kappa^{str}\begin{pmatrix} 1/4 & -\sqrt{3}/4 & 0 \\ -\sqrt{3}/4 & 3 & 0 \\ 0 & 0 & 0 \end{pmatrix}$.

Force constant matrices of three-body interaction from equation (19): $\Phi^{bend}(1,1) = -\kappa^{bend}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 6 & 0 \\ 0 & 0 & 0 \end{pmatrix}$,

$\Phi^{bend}(1,2) = -\kappa^{bend}\begin{pmatrix} 9/2 & -3\sqrt{3}/2 & 0 \\ -3\sqrt{3}/2 & 3/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ and $\Phi^{bend}(1,3) = -\kappa^{bend}\begin{pmatrix} 9/2 & 3\sqrt{3}/2 & 0 \\ 3\sqrt{3}/2 & 3/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$.

All force constant matrices of the atom '2' can be obtained from these matrices by applying a corresponding rotation operation on angle π around the axis perpendicular to the graphene plane. Using the derived force constant matrices I calculated the in-plane phonon dispersions of graphene in all high-symmetry crystallographic directions (see Figure 2).

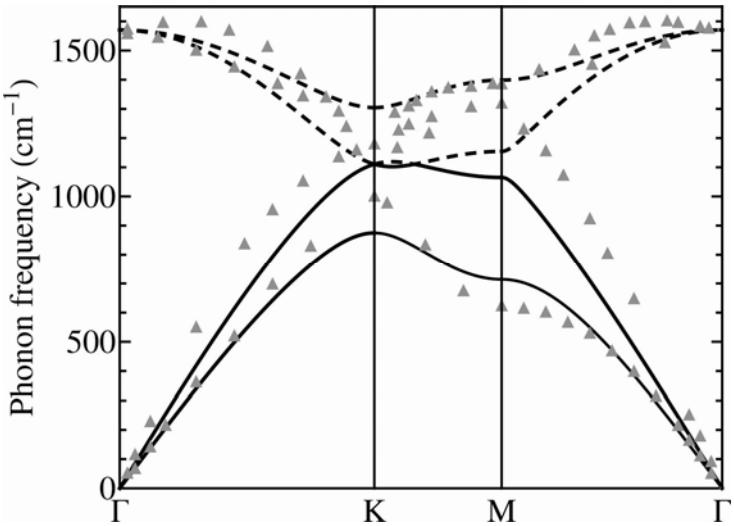

Fig.2. In-plane phonon branches of graphene. Solid lines denote acoustic branches and dashed lines denote optic branches. Gray triangles are experimental data for graphite taken from Ref. [7-8].

For values of the parameters κ^{str} =180.5 N/m and κ^{bend} =66.9 N/m it was obtained a reasonable agreement between calculated and experimental in-plane phonon frequencies.

Conclusions

Based on the Keating interatomic potential an analytical derivation of force constant matrices of two- and three-body interactions in crystals is performed. Using the derived force constant matrices the in-plane phonon energy spectra of graphene was calculated in the framework of a lattice dynamics theory. A reasonable agreement with experimental data was obtained. The results can extend the applicability of the current force constant models for investigation of crystal dynamics.

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