A simple model for the vibrational modes in honeycomb lattices

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The classical lattice dynamics of honeycomb lattices is studied in the harmonic approximation. Interactions between nearest neighbors are represented by springs connecting them. A short and necessary introduction of the lattice structure is presented. The dynamical matrix of the vibrational modes is then derived, and its eigenvalue problem is solved analytically. The solution may provide deeper insight into the nature of the vibrational modes. Numerical results for the vibrational frequencies are presented. To show that how effective our method used for the case of honeycomb lattice is, we also apply it to triangular and square lattice structures. A few suggested problems are listed in the concluding section.

I. INTRODUCTION

In crystals, atoms vibrate about their equilibrium position. Calculation of the vibrational frequencies and modes is an important and presently actively studied subject in solid-state physics. To interpret various properties of crystal lattices—for example, specific heat, thermal expansion coefficients, elastic constants—it is essential to take into account the lattice vibrations. Fortunately, several good textbooks of the subject are available (here we give just a small selection of the vast literature[1,2,3,4,5]), in which the quantum and classical treatments of lattice dynamics are presented lucidly. The vibration of the atoms depends on the interatomic interaction within the crystal. The interatomic interaction potential is often approximated by including only quadratic terms of the displacement of the atoms. This is called the *harmonic approximation*, and is the usual starting point for developing the theory of lattice dynamics. In the framework of classical mechanics, lattice dynamics can be treated through the equations of motion for the atoms. To determine the vibrational frequencies and the corresponding modes one needs to calculate the eigenvalues and the eigenvectors of the so-called dynamical matrix, which can be obtained from the interatomic interaction potential. If the dynamical matrix is known, the eigenvalue problem is straightforward, though only numerical solutions are available in many cases. Numerous texts[1,2,3,4,5,6,7] provide problems for the calculation of the vibrational modes in different crystal lattices. Fortunately, there are some well-known examples—such as linear chains with/without bases, square and cubic lattices—in which analytical methods can be used[1,2,3,4,5,6,7]. These examples are important for a deeper understanding of the theory of lattice dynamics.

In this paper we shall give another nontrivial example, namely the lattice dynamics of the honeycomb structure shown in Fig. 1. The classical lattice dynamics of the honeycomb lattice is modelled by using the harmonic approximation and assuming only nearest neighbor interactions between the atoms. In this simplest model the interaction between nearest neighbors can be represented by springs connecting them. It is assumed that black and white atoms have different masses, m_1 and m_2, respectively. The problem can be solved analytically and its solutions may provide insight into the nature of the vibrational modes. As it will be seen below, the analytical method is possible because of the symmetry properties of the honeycomb lattice. As a pre-requisite to the solution, a short and necessary introduction of the lattice structure is presented. More details on crystal structures can be found in many books on solid-state physics[1,2,3,4,5,8]. Finally, in connection with the honeycomb lattice, the intensive research on nanotubes[9] should be mentioned. Nanotubes are quasi-one-dimensional cylindrical structures in which a two-dimensional honeycomb lattice of crystalline graphite is rolled up into a cylinder. The work presented in this paper may serve as an introductory study of the far more complex lattice dynamics of graphite and nanotubes.

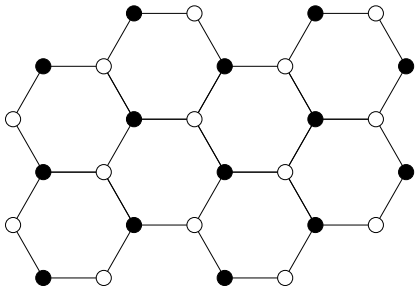

FIG. 1: Honeycomb lattice with two different atoms (black and white circles). The straight lines correspond to unstrained springs of force constant D connecting the nearest neighbor atoms in equilibrium state. The masses of the black and white atoms are m_1 and m_2.

The general method developed for calculating the vibration modes of honeycomb lattices proves to be useful for studying other lattice structures. Therefore, we shall present a few numerical results for the vibrational frequencies of equilateral triangular lattices and square lattices in which both the nearest neighbor and second nearest neighbor interactions are taken into account.

Our approach used in this paper may provide a didac-

tically useful examples for introducing the basic lattice dynamical notions developed in solid-state physics.

The rest of the text is organized as follows. In Sec. II a formula for the spring force acting on the atoms is derived. In Sec. III the description of the honeycomb lattice and the equations of motion for the atoms are given. In Sec. IV our analytic method for solving the eigenvalue problem is presented. In Sec. V some numerical results are mentioned. A few results are presented in Sec. VI for the case of triangular and square lattices. The conclusions and some suggested problems are given in Sec. VII.

II. THE FORCE

First, the force acting on an atom by a spring connecting the atoms is calculated. The springs are assumed to be ideal, ie. the spring force is proportional to the change in the spring's length. Denoting the vector between the two endpoints of the unstrained (strained) spring by $\mathbf{d}$ ($\mathbf{r}$), the change in the length of the spring is $|\mathbf{r}| - |\mathbf{d}|$. If the spring constant of the ideal springs is D then the restoring force is

$$\mathbf{F} = -D\left(|\mathbf{r}| - |\mathbf{d}|\right)\frac{\mathbf{r}}{|\mathbf{r}|}. \tag{1}$$

It is useful to express the force in terms of the displacement vector $\mathbf{u} = \mathbf{r} - \mathbf{d}$. In the harmonic approximation the strain of the spring is assumed to be small, ie. second order terms are neglected in $\mathbf{u}$. Explicitely: $|\mathbf{u}|/d = |\mathbf{r} - \mathbf{d}|/d \ll 1$. Thus, we have $|\mathbf{r}| = d\sqrt{1 + 2\frac{\mathbf{du}}{d^2} + \frac{\mathbf{u}^2}{d^2}} \approx d\left(1 + \frac{\mathbf{du}}{d^2}\right)$ and the force can be written as

$$\mathbf{F} = -D\,\frac{(\mathbf{du})\,\mathbf{d}}{d^2}. \tag{2}$$

It is convenient to define the outer or direct product $\mathbf{a}\otimes\mathbf{b}$ of two vectors $\mathbf{a}$ and $\mathbf{b}$[10,11]. This is a matrix whose α,β element is a product of the αth component of $\mathbf{a}$ and the βth component of $\mathbf{b}$, that is

$$(\mathbf{a}\otimes\mathbf{b})_{\alpha\beta} = a^*_\alpha b_\beta, \tag{3}$$

where * denotes the complex conjugation (of complex vectors). The following direct-product identities will prove useful in the calculations below:

$$(\mathbf{a}\otimes\mathbf{b})\,\mathbf{c} \;=\; \mathbf{a}\,(\mathbf{bc}), \tag{4a}$$

$$(\mathbf{a}\otimes\mathbf{b})(\mathbf{c}\otimes\mathbf{d}) \;=\; (\mathbf{bc})\,\mathbf{a}\otimes\mathbf{d}. \tag{4b}$$

In direct-product notation, the (2) force can be rewritten as

$$\mathbf{F} = -D\,\frac{\mathbf{d}\otimes\mathbf{d}}{d^2}\,\mathbf{u}. \tag{5}$$

From this form it is clearly seen that the force in the harmonic approximation is proportional to the displacement vector $\mathbf{u}$, and that the constant of proportionality is the product of the spring constant D and the direct product of the unit vector $\mathbf{d}/|\mathbf{d}|$ with itself. In the following section the equations of motion of the atoms are formulated by using the above form of the spring force acting on the atoms.

III. THE EQUATIONS OF MOTION

In Fig. 1 the position vector $\mathbf{R}$ of the black atoms in the honeycomb structure can be given in the form

$$\mathbf{R} = j_1\mathbf{a}_1 + j_2\mathbf{a}_2, \tag{6}$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the independent primitive translation vectors shown in Fig. 2, while j_1 and j_2 range through all integer values (i.e. positive and negative integers, as well as zero). The primitive translation vectors have the same magnitude $|\mathbf{a}_1| = |\mathbf{a}_2| = \sqrt{3}a$, where $a = |\mathbf{d}_1|$ is the length of hexagons' side. The primitive cell of the honeycomb lattice can be chosen as the parallelogram whose non-parallel sides are the two primitive translation vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ (in Fig. 2 the sides of the parallelogram are $\mathbf{a}_1$, $\mathbf{a}_2$ and the two dotted lines). In the honeycomb lattice each primitive cell with a *two-point basis* contains two atoms (black and white circles in Fig. 1); one is at the common starting point of vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, while the other one is at $1/3(\mathbf{a}_1 + \mathbf{a}_2)$ in Fig. 2.

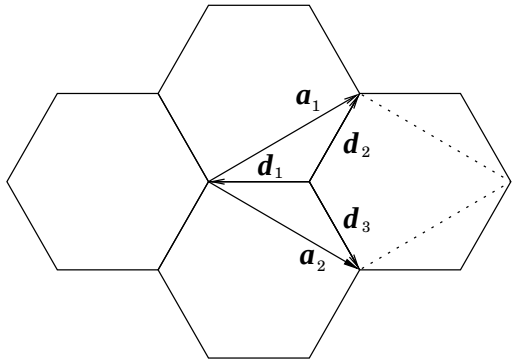

FIG. 2: The primitive translation vectors of the honeycomb lattice are vectors $\mathbf{a}_1$ and $\mathbf{a}_2$; the primitive cell is a parallelogram whose sides are these two vectors and the two dotted lines. The three vectors $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3$ will be useful in the calculations below.

It is useful to introduce three unit vectors $(\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3)$ by

$$\mathbf{n}_i = \frac{\mathbf{d}_i}{|\mathbf{d}_i|}\ ,\ i = 1, 2, 3. \tag{7}$$

The vectors $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3$, are shown in Fig. 2; their magnitude is $|\mathbf{d}_i| = a$. Thus, the primitive translation vectors are $\mathbf{a}_1 = \mathbf{d}_2 - \mathbf{d}_1 = a(\mathbf{n}_2 - \mathbf{n}_1)$ and $\mathbf{a}_2 = \mathbf{d}_3 - \mathbf{d}_1 = a(\mathbf{n}_3 - \mathbf{n}_1)$. Later on the following identities for vector $\mathbf{n}$

will frequently be used:

$$\sum_{j=1}^{3} \mathbf{n}_j = 0, \tag{8a}$$

$$\sum_{j=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_j = \frac{3}{2}\,\mathbf{E}, \tag{8b}$$

$$(\mathbf{n}_j \mathbf{n}_k) = \begin{cases} 1 & \text{if } j = k, \\ -\frac{1}{2} & \text{if } j \neq k, \end{cases} \tag{8c}$$

and $\mathbf{E}$ is the 2×2 unit matrix.

The displacements of the two atoms in the primitive cell specified by the lattice vector $\mathbf{R}$ are denoted by $\mathbf{u}(\mathbf{R})$ and $\mathbf{v}(\mathbf{R})$. From (5) it can be shown that the components of the displacements perpendicular to the plane do not contribute to the force in the harmonic approximation. Each atom interacts with its three neighbors. Denoting the masses of the two basis atoms by m_1 and m_2, and using (5) for the spring force acting on the atoms, the following equations of motion are obtained for $\mathbf{u}(\mathbf{R})$ and $\mathbf{v}(\mathbf{R})$:

$$m_1\,\ddot{\mathbf{u}}(\mathbf{R}) = -D\,\mathbf{n_1} \otimes \mathbf{n_1}\left[\mathbf{u}(\mathbf{R}) - \mathbf{v}(\mathbf{R})\right] - D\,\mathbf{n_2} \otimes \mathbf{n_2}\left[\mathbf{u}(\mathbf{R}) - \mathbf{v}(\mathbf{R} - \mathbf{a}_1)\right] - D\,\mathbf{n_3} \otimes \mathbf{n_3}\left[\mathbf{u}(\mathbf{R}) - \mathbf{v}(\mathbf{R} - \mathbf{a}_2)\right], \tag{9a}$$

$$m_2\,\ddot{\mathbf{v}}(\mathbf{R}) = -D\,\mathbf{n_1} \otimes \mathbf{n_1}\left[\mathbf{v}(\mathbf{R}) - \mathbf{u}(\mathbf{R})\right] - D\,\mathbf{n_2} \otimes \mathbf{n_2}\left[\mathbf{v}(\mathbf{R}) - \mathbf{u}(\mathbf{R} + \mathbf{a}_1)\right] - D\,\mathbf{n_3} \otimes \mathbf{n_3}\left[\mathbf{v}(\mathbf{R}) - \mathbf{u}(\mathbf{R} + \mathbf{a}_2)\right]. \tag{9b}$$

Eq. (9) is an infinite set of equations for the displacements $\mathbf{u}(\mathbf{R})$ and $\mathbf{v}(\mathbf{R})$. Following the traditional method, we seek a solution representing a wave of angular frequency $\omega(\mathbf{q})$ and wave vector $\mathbf{q}$:

$$\mathbf{u}(\mathbf{R}) = \frac{\mathbf{u}(\mathbf{q})}{\sqrt{m_1}}\, e^{i\omega(\mathbf{q})t + i\mathbf{q}\mathbf{R}}, \tag{10a}$$

$$\mathbf{v}(\mathbf{R}) = \frac{\mathbf{v}(\mathbf{q})}{\sqrt{m_2}}\, e^{i\omega(\mathbf{q})t + i\mathbf{q}\mathbf{R}}, \tag{10b}$$

where the vectors $\mathbf{u}(\mathbf{q})$ and $\mathbf{v}(\mathbf{q})$ are to be determined, and $\mathbf{q}$ is in the first Brillouin zone. The usual Born-von Kármán periodic boundary conditions are applied[1,2,3,4,5,8], i.e. $\mathbf{u}(\mathbf{R} + N_i\mathbf{a}_i) = \mathbf{u}(\mathbf{R})$ and $\mathbf{v}(\mathbf{R} + N_i\mathbf{a}_i) = \mathbf{v}(\mathbf{R})$, where N_1 and N_2 are large integers whose product $N_1 N_2 = N$ is the total number of primitive cells within the crystal. The periodic boundary conditions restrict the allowed wave vectors $\mathbf{q}$ in Eq. (10) to the form:

$$\mathbf{q} = \frac{p_1}{N_1}\mathbf{b}_1 + \frac{p_2}{N_2}\mathbf{b}_2, \tag{11}$$

where p_1 and p_2 are integers, and the $\mathbf{b}_j$ are the reciprocal lattice vectors defined by $\mathbf{a}_i\mathbf{b}_j = 2\pi\delta_{ij}$, $i, j = 1, 2$. It is convenient to choose p_1, p_2 such that $\mathbf{q}$ is limited to the first Brillouin zone. For example, if N_1 and N_2 are even integers (which will be irrelevant in the limit $N \to \infty$), $-N_i/2 \leq p_i < N_i/2$ $(i = 1, 2)$. More details on the concept of the Brillouin zone can be found in many books on solid-state physics[1,2,3,4,5,8].

Substitution of the solutions (10) into the equations of motion (9) leads to an eigenvalue problem:

$$\mathbf{D}(\mathbf{q}) \begin{bmatrix} \mathbf{u}(\mathbf{q}) \\ \mathbf{v}(\mathbf{q}) \end{bmatrix} = \omega^2(\mathbf{q}) \begin{bmatrix} \mathbf{u}(\mathbf{q}) \\ \mathbf{v}(\mathbf{q}) \end{bmatrix}, \tag{12}$$

where

$$\mathbf{D}(\mathbf{q}) = \begin{bmatrix} \mathbf{D}_{11}(\mathbf{q}) & \mathbf{D}_{12}(\mathbf{q}) \\ \mathbf{D}_{21}(\mathbf{q}) & \mathbf{D}_{22}(\mathbf{q}) \end{bmatrix}, \tag{13a}$$

$$\mathbf{D}_{11}(\mathbf{q}) = \frac{D}{m_1}\sum_{j=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_j = \frac{3D}{2m_1}\mathbf{E}, \tag{13b}$$

$$\mathbf{D}_{22}(\mathbf{q}) = \frac{D}{m_2}\sum_{j=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_j = \frac{3D}{2m_2}\mathbf{E}, \tag{13c}$$

$$\mathbf{D}_{12}(\mathbf{q}) = -\frac{D}{\sqrt{m_1 m_2}} e^{i\mathbf{q}\mathbf{d}_1} \sum_{j=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_j\, e^{-i\mathbf{q}\mathbf{d}_j}, \tag{13d}$$

$$\mathbf{D}_{21}(\mathbf{q}) = [\mathbf{D}_{12}(\mathbf{q})]^*. \tag{13e}$$

In the last equality of (13b) and (13c) we used Eq. (8b). The matrix $\mathbf{D}(\mathbf{q})$ is commonly called the *dynamical matrix*. The eigenvectors of the dynamical matrix are the unknown vectors $\mathbf{u}(\mathbf{q})$ and $\mathbf{v}(\mathbf{q})$ of Eq. (10). In our case, $\mathbf{D}(\mathbf{q})$ is a 4×4 matrix, while the $\mathbf{D}_{ij}(\mathbf{q})$ are 2×2 matrices $(i, j = 1, 2)$. For a given $\mathbf{q}$ there are 4 eigenfrequencies and 4 corresponding, mutually orthogonal eigenvectors, which give the amplitudes of the wave solutions (10). In the literature these eigenvectors are called *vibrational modes*.

The eigenfrequencies can be found by solving the following equation for $\lambda(\mathbf{q}) = \omega^2(\mathbf{q})$:

$$\det\left[\mathbf{D}(\mathbf{q}) - \lambda(\mathbf{q})\,\mathbf{I}\right] = 0, \tag{14}$$

where $\mathbf{I}$ is the 4×4 unit matrix. The 4×4 determinant can be evaluated directly; this is, however, rather tedious. Below we present another approach, which allows us to find analytical solutions for the eigenfrequencies. Note that the dynamical matrix is hermitian (see Eq. (13e)),

therefore its eigenvalues are real. The basic idea is that $\mathbf{D}(\mathbf{q})$ is a block matrix, whose elements are the 2×2 matrices $\mathbf{D}_{ij}(\mathbf{q})$, and $\mathbf{D}_{11}(\mathbf{q})$ and $\mathbf{D}_{22}(\mathbf{q})$ are diagonal. This way, the original eigenvalue problem is reduced to finding the eigenvalues of a 2×2 matrix. This problem can be solved analytically.

IV. ANALYTIC SOLUTION OF THE EIGENVALUE PROBLEM

In this section an analytic method is presented to determine the eigenfrequencies and the vibrational modes of the honeycomb structure. Since $\mathbf{D}_{11}(\mathbf{q})$ and $\mathbf{D}_{22}(\mathbf{q})$ are diagonal matrices, one can eliminate $\mathbf{u}(\mathbf{q})$ from Eq. (12), and find by using Eqs. (13b)-(13c)

$$\mathbf{P}\mathbf{P}^*\mathbf{v}(\mathbf{q}) = \overline{\lambda}(\mathbf{q})\,\mathbf{v}(\mathbf{q}), \quad \text{where} \tag{15a}$$

$$\mathbf{P} = \sum_{j=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_j\, e^{i\mathbf{q}\mathbf{d}_j}, \tag{15b}$$

$$\overline{\lambda}(\mathbf{q}) = \frac{m_1 m_2}{D^2}\left(\lambda(\mathbf{q}) - \frac{3D}{2m_1}\right)\left(\lambda(\mathbf{q}) - \frac{3D}{2m_2}\right). \tag{15c}$$

Eq. (15a) is another eigenvalue equation. The matrix $\mathbf{P}\mathbf{P}^*$ can be rewritten as

$$\begin{aligned}
\mathbf{P}\mathbf{P}^* &= \sum_{j,k=1}^{3} \left[(\mathbf{n}_j \otimes \mathbf{n}_j)\,(\mathbf{n}_k \otimes \mathbf{n}_k)\right] e^{i\mathbf{q}(\mathbf{d}_j - \mathbf{d}_k)} \\
&= \sum_{j,k=1}^{3} \left[(\mathbf{n}_j \otimes \mathbf{n}_k)\,(\mathbf{n}_j \mathbf{n}_k)\right] e^{i\mathbf{q}(\mathbf{d}_j - \mathbf{d}_k)} \\
&= \sum_{j=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_j - \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^{3} \mathbf{n}_j \otimes \mathbf{n}_k e^{i\mathbf{q}(\mathbf{d}_j - \mathbf{d}_k)} \\
&= \frac{3}{2} \sum_{j=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_j - \frac{1}{2} \sum_{j,k=1}^{3} \mathbf{n}_j \otimes \mathbf{n}_k e^{i\mathbf{q}(\mathbf{d}_j - \mathbf{d}_k)} \\
&= \frac{9}{4}\,\mathbf{E} - \frac{1}{2}\,\mathbf{f} \otimes \mathbf{f},
\end{aligned} \tag{16}$$

where

$$\mathbf{f} = \sum_{j=1}^{3} \mathbf{n}_j e^{i\mathbf{q}\mathbf{d}_j}. \tag{17}$$

In the derivation, identities (4b), (8b) and (8c) have been used. Note that $\mathbf{f}$ is a complex vector.

From (4a) it is easy to see that $\mathbf{v}_1 = \mathbf{f}$ is an eigenvector of the matrix $\mathbf{P}\mathbf{P}^*$:

$$\mathbf{P}\mathbf{P}^*\mathbf{v}_1 = \mathbf{P}\mathbf{P}^*\mathbf{f} = \frac{9}{4}\,\mathbf{f} - \frac{1}{2}\,\mathbf{f}^2\,\mathbf{f} = \left(\frac{9}{4} - \frac{1}{2}\,\mathbf{f}^2\right)\mathbf{v}_1, \tag{18}$$

with eigenvalue $\overline{\lambda}_1 = 9/4 - 1/2\,\mathbf{f}^2$. Using (8c), the dot product $\mathbf{f}^2$ can easily be evaluated:

$$\begin{aligned}
\mathbf{f}^2 &= \sum_{j,k=1}^{3} (\mathbf{n}_j \mathbf{n}_k) e^{-i\mathbf{q}\mathbf{d}_j + i\mathbf{q}\mathbf{d}_k} = 3 - \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^{3} e^{i\mathbf{q}(\mathbf{d}_k - \mathbf{d}_j)} \\
&= 3 - \eta(\mathbf{q}),
\end{aligned} \tag{19}$$

where

$$\eta(\mathbf{q}) = \cos \mathbf{q}\mathbf{a}_1 + \cos \mathbf{q}\mathbf{a}_2 + \cos \mathbf{q}(\mathbf{a}_1 - \mathbf{a}_2), \tag{20}$$

has been expressed in terms of the primitive translation vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Thus, the eigenvalue $\overline{\lambda}_1$ corresponding to the eigenvector $\mathbf{v}_1$ is

$$\overline{\lambda}_1 = \frac{3 + 2\eta(\mathbf{q})}{4}. \tag{21}$$

The other eigenvector must be perpendicular to $\mathbf{v}_1$. It is useful to introduce three unit vectors, $\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$ (see Fig. 3), such that

$$\mathbf{l}_j \mathbf{n}_j = 0, \tag{22a}$$

$$\mathbf{l}_j \mathbf{n}_k = -\mathbf{l}_k \mathbf{n}_j, \tag{22b}$$

$$|\,\mathbf{l}_j \mathbf{n}_k\,| = \frac{\sqrt{3}}{2}, \ \text{if} \ j \neq k. \tag{22c}$$

Next, the vector

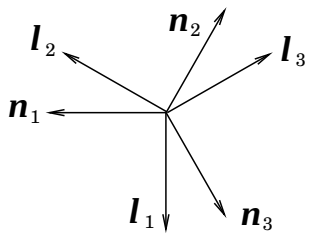

FIG. 3: The three vectors $\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$ are obtained by a 90°-rotation from $\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3$.

$$\mathbf{g} = \sum_{j=1}^{3} \mathbf{l}_j e^{-i\mathbf{q}\mathbf{d}_j}. \tag{23}$$

is defined. Note the presence of the vectors $\mathbf{d}_j$ in the exponent. Then, from (22) it is obvious that $\mathbf{g}$ is perpendicular to the vector $\mathbf{f}$:

$$\mathbf{f}\,\mathbf{g} = \sum_{j,k=1}^{3} \mathbf{n}_j \mathbf{l}_k e^{-i\mathbf{q}\mathbf{d}_j - i\mathbf{q}\mathbf{d}_k} = 0. \tag{24}$$

Therefore, the other eigenvector of $\mathbf{P}\mathbf{P}^*$ can be chosen as $\mathbf{v}_2 = \mathbf{g}$, and the corresponding eigenvalue $\overline{\lambda}_2$ can be found from $\mathbf{P}\mathbf{P}^*\mathbf{v}_2 = \mathbf{P}\mathbf{P}^*\mathbf{g} = \frac{9}{4}\,\mathbf{g} - \frac{1}{2}\,\mathbf{f}\,(\mathbf{f}\,\mathbf{g}) = \frac{9}{4}\,\mathbf{v}_2$. Thus, the second eigenvalue is

$$\overline{\lambda}_2 = \frac{9}{4}. \tag{25}$$

Note that this eigenvalue is independent of $\mathbf{q}$. Finally, using (15c) one can obtain the four eigenfrequencies of the dynamical matrix $\mathbf{D}(\mathbf{q})$:

$$\omega_{1,2}(\mathbf{q}) \;=\; \sqrt{\lambda_{1,2}(\mathbf{q})} = \sqrt{\frac{3}{4}\,D\left[\frac{1}{m_1}+\frac{1}{m_2} \pm \sqrt{\left(\frac{1}{m_1}-\frac{1}{m_2}\right)^2+\frac{12+8\,\eta(\mathbf{q})}{9\,m_1 m_2}}\right]}, \tag{26a}$$

$$\omega_3(\mathbf{q}) \;=\; \sqrt{\lambda_3(\mathbf{q})}=0 \quad \text{and} \quad \omega_4(\mathbf{q}) = \sqrt{\lambda_4(\mathbf{q})} = \sqrt{\frac{3}{2}D\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}, \tag{26b}$$

where λ_1 and λ_2 ($\pm$ signs, respectively) correspond to $\overline{\lambda}_1$, while λ_3 and λ_4 to $\overline{\lambda}_2$. $\eta(\mathbf{q})$ is defined in (20).

To find $\mathbf{u}(\mathbf{q})$ one can use Eqs. (12) and (13b)-(13c), and obtain

$$\mathbf{u}(\mathbf{q}) = -\frac{D/\sqrt{m_1 m_2}}{\lambda(\mathbf{q}) - 3D/\left(2m_1\right)}\, e^{i\mathbf{q}\mathbf{d}_1}\mathbf{P}^*\mathbf{v}(\mathbf{q}). \tag{27}$$

First, $\mathbf{P}^*\mathbf{v}_1$ and $\mathbf{P}^*\mathbf{v}_2$ are calculated. Using (4a), (8a) and (8c)

$$\begin{aligned}\mathbf{P}^*\mathbf{v}_1 \;&=\; \mathbf{P}^*\mathbf{f} = \sum_{j=1}^{3}\mathbf{n}_j\otimes\mathbf{n}_j e^{-i\mathbf{q}\mathbf{d}_j}\sum_{k=1}^{3}\mathbf{n}_k e^{i\mathbf{q}\mathbf{d}_k}\\ &=\; \sum_{j=1}^{3}\mathbf{n}_j - \frac{1}{2}\sum_{\substack{j,k=1\\ j\neq k}}^{3}\mathbf{n}_j e^{i\mathbf{q}(\mathbf{d}_k-\mathbf{d}_j)}\\ &=\; -\frac{1}{2}\sum_{k=1}^{3}e^{i\mathbf{q}\mathbf{d}_k}\sum_{j=1}^{3}\mathbf{n}_j e^{-i\mathbf{q}\mathbf{d}_j} = c\,\mathbf{f}^*,\end{aligned} \tag{28}$$

where $c = -\frac{1}{2}\sum_{k=1}^{3} e^{i\mathbf{q}\mathbf{d}_k}$ is a scalar value depending on $\mathbf{q}$. Similarly,

$$\begin{aligned}\mathbf{P}^*\mathbf{v}_2 \;&=\; \mathbf{P}^*\mathbf{g} = \sum_{j=1}^{3}\mathbf{n}_j\otimes\mathbf{n}_j e^{-i\mathbf{q}\mathbf{d}_j}\sum_{k=1}^{3}\mathbf{l}_k e^{-i\mathbf{q}\mathbf{d}_k}\\ &=-\frac{3}{2}\left(\mathbf{l}_1 e^{i\mathbf{q}\mathbf{d}_1}+\mathbf{l}_2 e^{i\mathbf{q}\mathbf{d}_2}+\mathbf{l}_3 e^{i\mathbf{q}\mathbf{d}_3}\right) = -\frac{3}{2}\,\mathbf{g}^*,\end{aligned} \tag{29}$$

where we have made use of the identities $\mathbf{n}_2-\mathbf{n}_1=\sqrt{3}\,\mathbf{l}_3$, $\mathbf{n}_3-\mathbf{n}_2=\sqrt{3}\,\mathbf{l}_1$, $\mathbf{n}_1-\mathbf{n}_3=\sqrt{3}\,\mathbf{l}_2$ and $\mathbf{d}_1+\mathbf{d}_2+\mathbf{d}_3=0$. Finally, using Eqs. (27)-(29) the four eigenvectors are

$$\omega_1 \;\rightarrow \begin{bmatrix}-c\,C_1(\mathbf{q})\;\mathbf{f}^*\\ \mathbf{f}\end{bmatrix},\;\; \omega_2 \rightarrow \begin{bmatrix}-c\,C_2(\mathbf{q})\;\mathbf{f}^*\\ \mathbf{f}\end{bmatrix}, \tag{30a}$$

$$\omega_3 \;\rightarrow \begin{bmatrix}-\sqrt{\frac{m_1}{m_2}}\,\mathbf{g}^* e^{i\mathbf{q}\mathbf{d}_1}\\ \mathbf{g}\end{bmatrix},\;\; \omega_4 \rightarrow \begin{bmatrix}\sqrt{\frac{m_2}{m_1}}\,\mathbf{g}^* e^{i\mathbf{q}\mathbf{d}_1}\\ \mathbf{g}\end{bmatrix}, \tag{30b}$$

$$\text{where}\;\; C_i(\mathbf{q}) = \frac{D/\sqrt{m_1 m_2}}{\lambda_i - 3D/\left(2m_1\right)}\, e^{i\mathbf{q}\mathbf{d}_1}, \tag{30c}$$

and $\mathbf{f}$, $\mathbf{g}$, λ_i, and c are functions of $\mathbf{q}$ defined in Eqs. (17), (23), (26) and after Eq. (28), respectively. It can be shown that the four eigenvectors are mutually orthogonal.

It is also worth mentioning that the eigenmode corresponding to $\omega_3(\mathbf{q}) = 0$ is a special one, for example, $[\mathbf{u}(\mathbf{R}) - \mathbf{v}(\mathbf{R})]\,\mathbf{n}_1 = 0$ for this mode. This can easily be proved by using (10) and the expression for the ω_3 eigenmode given by (30b). This means that neglecting the second order terms in the displacements $\mathbf{u}(\mathbf{R})$ and $\mathbf{v}(\mathbf{R})$ all springs are *unstrained*, ie. their lengths remain a. The atoms of the whole lattice move as if the spring system were a universal joint. This movement of the atoms does not require any energy (the eigenfrequency is zero), therefore there is no resistance to a shear of the lattice. Consequently, the stability of the lattice is lost, and the whole honeycomb structure becomes *unstable*. In nature, besides the central interaction between nearest neighbors there exist n^{th} neighbor ($n = 2, 3, \cdots$) and lateral interactions as well[4,9]. In the latter case, the interatomic interaction energy depends on the angle between two adjacent bonds. Such interactions give rise to the so-called *bond-bending forces*. These additional interactions stabilize the lattice and one must take them into account to calculate the vibrational modes more accurately. Nanotubes provide a good example for this[9].

V. NUMERICAL RESULTS

In this section a few numerical results for the eigenfrequencies are presented. As it is seen from (26) only $\omega_1(\mathbf{q})$ and $\omega_2(\mathbf{q})$ have nontrivial $\mathbf{q}$-dependence. In Figs. 4 and 5 the contour plot of $\omega_1(\mathbf{q})$ and $\omega_2(\mathbf{q})$ are shown for $m_1/m_2 = 2$. The vector $\mathbf{q} = (q_x, q_y)$ is taken in a Cartesian coordinate system in which the x-axis is parallel to the direction of the vector $-\mathbf{d}_1$. In these contour plots the lines show the constant eigenfrequencies in the parameter space $\mathbf{q} = (q_x, q_y)$. It is seen from the figures that $\omega_1(\mathbf{q})$ has a deep minimum (zero) at $\mathbf{q} = 0$, while $\omega_2(\mathbf{q})$ has a maximum there, equal to $\omega_4 = \sqrt{3D(1/m_1 + 1/m_2)/2}$ for arbitrary mass ratio m_1/m_2. The contour plot is also a useful representation of the vibrational modes to show the symmetries of the eigenfrequencies in the $\mathbf{q}$ space. One can see from Figs. 4 and 5 that both $\omega_1(\mathbf{q})$ and $\omega_2(\mathbf{q})$ have, eg. a 60° rotation around the axis which goes through the point $\mathbf{q} = 0$ and perpendicular to the (q_x, q_y) plane.

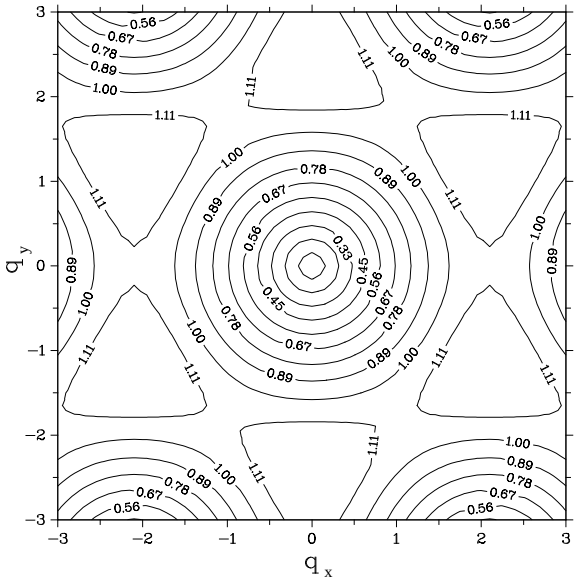

FIG. 4: The contour plot of $\omega_1(\mathbf{q})$ (in units of $\sqrt{D/m_1}$) versus $\mathbf{q}$ (in units of $1/a$) for $m_1/m_2 = 2$. q_x is parallel to the vector $-\mathbf{d}_1$.

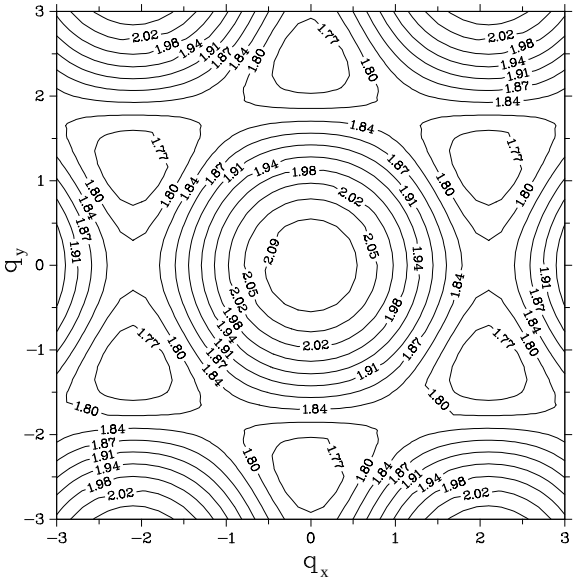

FIG. 5: The same contour plot as in Fig. 4 for $\omega_2(\mathbf{q})$.

In Fig. 6 the eigenfrequencies $\omega_1(\mathbf{q})$, $\omega_2(\mathbf{q})$ and $\omega_4(\mathbf{q})$ are plotted along the lines in the first Brillouin zone joining the points Γ, M and K shown in the inset of the figure. In solid-state physics it is a common practice to plot the eigenfrequencies along the lines between high symmetric points. Owing to the symmetry properties of the eigenfrequency in the $\mathbf{q}$ space it is enough to calculate the eigenfrequencies only inside the area enlosed by these lines. In the same Cartesian coordinate system as in Fig. 4 the points Γ, M and K are $\mathbf{q}_\Gamma = 0$, $\mathbf{q}_\mathrm{M} = (\frac{2\pi}{3a}, 0)$ and $\mathbf{q}_\mathrm{K} = (\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a})$, respectively. Here a is the length of hexagons' side. Note that $\omega_4(\mathbf{q})$ is independent of $\mathbf{q}$.

In the literature the vibrational mode corresponding to $\omega_1(\mathbf{q})$ is called the *acoustical branch* because the eigenfrequency at small $|\mathbf{q}|$ has the same form as that of the sound waves, namely $\omega = v|\mathbf{q}|$, where v is the sound velocity. Those vibrational modes for which the frequencies does not tend to zero as $|\mathbf{q}| \to 0$ form the *optical branch*. In our example $\omega_2(\mathbf{q})$ and $\omega_4(\mathbf{q})$ belong to the optical branch. It is clear from Fig. 6 that at the point K there is a frequency gap between the acoustical and optical branch. This gap is equal to $\sqrt{\frac{3D}{2}}\left|1/\sqrt{m_1} - 1/\sqrt{m_2}\right|$.

We now take $m_1 = m_2$ corresponding to a single graphite layer. A similar plot as in Fig. 6 is shown in Fig. 7 for this case. One can see that the gap disappears. These results are similar to those obtained from the recent accurate calculations for two modes of the isolated graphite layer[12].

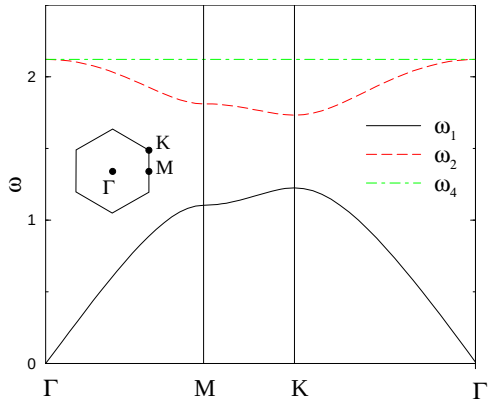

FIG. 6: The eigenfrequencies (in units of $\sqrt{D/m_1}$) $\omega_1(\mathbf{q})$ (solid), $\omega_2(\mathbf{q})$ (dashed), $\omega_4(\mathbf{q})$ (dot-dashed) along lines between points Γ, M and K. These points are in the first Brillouin zone shown in the inset. The mass ratio is $m_1/m_2 = 2$.

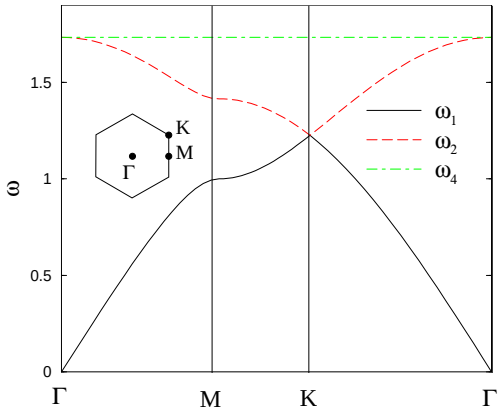

FIG. 7: The same plot as in Fig. 6 for $m_1/m_2 = 1$.

VI. OTHER LATTICE STRUCTURES

To demonstrate the effectivity of the general method developed in Sections II and III, we now present further examples of lattice structures.

In Fig. 8 an equilateral triangular lattice is shown. We assume only nearest neighbor interactions repersented by springs of force constant D. One can easily write

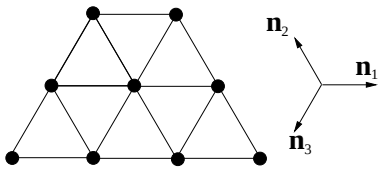

FIG. 8: Equilateral triangular lattice with nearest neighbor interactions. The straight solid lines correspond to unstrained springs of force constant D connecting nearest neighbor atoms in equilibrium state. The unit vectors $\mathbf{n}_1, \mathbf{n}_2$ and $\mathbf{n}_3$ correspond to the directions of the unstrained springs of length a.

down the equations of motion for the displacements of the atoms using Eq. (5) and it yields the 2×2 dynamical matrix:

$$\mathbf{D}(\mathbf{q}) = \frac{2D}{m} \sum_{i=1}^{3} \left[1 - \cos\left(\mathbf{q}\,\mathbf{n}_i\, a\right)\right] \mathbf{n}_i \otimes \mathbf{n}_i, \qquad (31)$$

where the unit vectors $\mathbf{n}_i$ $(i = 1, 2, 3)$ are shown in Fig. 8.

The eigenfrequencies are again the square-root of the eigenvalues of the dynamical matrix as in (14). From a simple calculation one finds

$$\omega_{1,2}(\mathbf{q}) = \sqrt{\frac{D_{11} + D_{22} \pm \sqrt{\left(D_{11} - D_{22}\right)^2 + 4D_{12}^2}}{2}}, \qquad (32)$$

where D_{ij} is the ij matrix element of the 2×2 dynamical matrix $\mathbf{D}(\mathbf{q})$ for a given wave vector $\mathbf{q}$. In Fig. 9 the eigenfrequencies $\omega_1(\mathbf{q})$ and $\omega_2(\mathbf{q})$ are plotted along the lines in the first Brillouin zone joining the points Γ, K and M shown in the figure. In the Cartesian coordinate system in which q_x is parallel to the unit vector $\mathbf{n}_1$, the points Γ, X and M are $\mathbf{q}_\Gamma = 0$, $\mathbf{q}_\mathrm{K} = (\frac{4\pi}{3a}, 0)$ and $\mathbf{q}_\mathrm{M} = (\frac{\pi}{a}, \frac{\pi}{\sqrt{3}a})$, respectively.

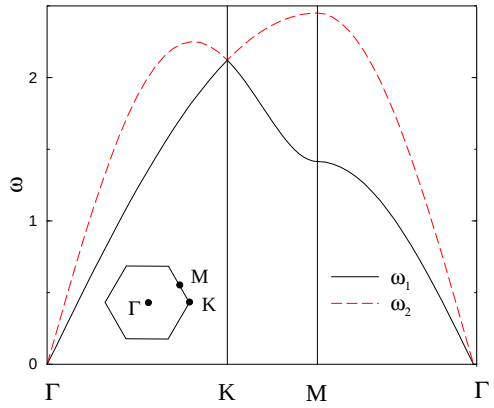

FIG. 9: For triangular lattice the eigenfrequencies (in units of $\sqrt{D/m}$) $\omega_1(\mathbf{q})$ (solid) and $\omega_2(\mathbf{q})$ (dashed) along lines between points Γ, K and M. These points are in the first Brillouin zone shown in the inset.

In Fig. 10 a square lattice is shown. We now assume first and second nearest neighbor interactions (solid and dashed lines in the figure) represented by springs of force constant D_1 and D_2, respectively. Similar way as before,

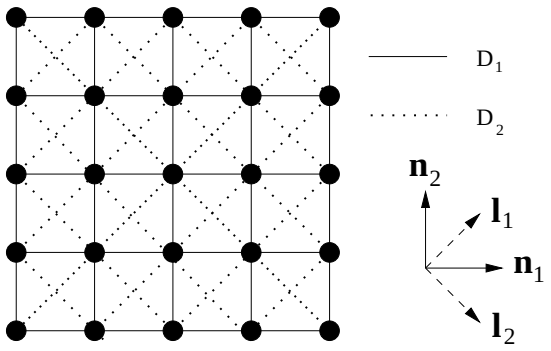

FIG. 10: Square lattice with first and second nearest interactions. The straight lines correspond to unstrained springs of force constant D_1 (solid lines) and D_2 (dashed lines) connecting first and second nearest neighbor atoms in equilibrium state. The distance between nearest neighbors is a. The unit vectors $\mathbf{n}_1, \mathbf{n}_2, \mathbf{l}_1$ and $\mathbf{l}_2$ correspond to the directions of the unstrained springs.

one finds that the 2×2 dynamical matrix is

$$\mathbf{D}(\mathbf{q}) = \frac{2D_1}{m} \sum_{i=1}^{2} \left[1 - \cos\left(\mathbf{q}\,\mathbf{n}_i\, a\right)\right] \mathbf{n}_i \otimes \mathbf{n}_i + \frac{2D_2}{m} \sum_{i=1}^{2} \left[1 - \cos\left(\mathbf{q}\,\mathbf{l}_i \sqrt{2}\, a\right)\right] \mathbf{l}_i \otimes \mathbf{l}_i, \qquad (33)$$

where the unit vectors $\mathbf{n}_i$ and $\mathbf{l}_i$ $(i = 1, 2)$ are shown in

Fig. 10. Finally, the two eigenfrequencies can be obtained again from Eq. (32). In Fig. 11 the eigenfrequencies $\omega_1(\mathbf{q})$ and $\omega_2(\mathbf{q})$ are plotted along the lines in the first Brillouin zone joining the points Γ, X and M shown in the figure. In the Cartesian coordinate system in which q_x is parallel to the unit vector $\mathbf{n}_1$, the points Γ, X and M are $\mathbf{q}_\Gamma = 0$, $\mathbf{q}_\mathrm{X} = (\frac{\pi}{a}, 0)$ and $\mathbf{q}_\mathrm{M} = (\frac{\pi}{a}, \frac{\pi}{a})$, respectively.

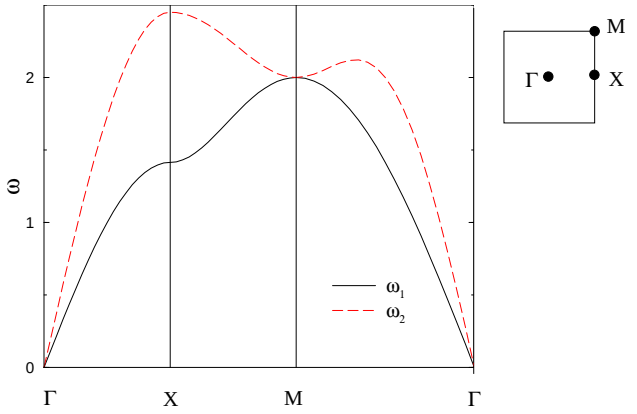

FIG. 11: For square lattice the eigenfrequencies (in units of $\sqrt{D_1/m}$) $\omega_1(\mathbf{q})$ (solid) and $\omega_2(\mathbf{q})$ (dashed) along lines between points Γ, X and M. These points are in the first Brillouin zone shown on the right of the figure. The ratio of the force constants is $D_1/D_2 = 2$.

VII. CONCLUSIONS

We first calculated the vibrational modes of the honeycomb lattice in the harmonic approximation. It was assumed that nearest neighbor atoms are connected by ideal springs. Using the direct product of vectors we derived a formula for the spring force acting on an atom. The equations of motion for the atoms were then derived and the resulting dynamical matrix was given explicitly. The vibrational frequencies and modes were determined from the eigenvalue problem of the dynamical matrix by analytic methods. Our work may provide a starting point to the studies of the more complicated lattice dynamics of nanotubes. Our general approach is also applied to study the lattice dynamics of the equilateral triangular and the square lattices. In the latter case, to investigate more complicated structures, not only the first but the second nearest neighbor interactions are also included.

Finally, we mention some problems.

- What is the first Brillouin zone for the square, triangular and honeycomb lattice structures discussed before? Study the symmetry properties of the eigenfrequencies $\omega_1(\mathbf{q})$ and $\omega_2(\mathbf{q})$ in the first Brillouin zone.
- Study the long wavelength limit, that is when $|\mathbf{q}|a \ll 1$ for the square, triangular and honeycomb lattice structures. What are the eigenmodes in this case? Determine the sound velocity.
- In Fig. 12 a and b two ladder-type lattices are shown. Using the method developed in Sections II and III find the vibrational frequencies and modes for these lattices. Determine how the results depend on α in Fig. 12 b.

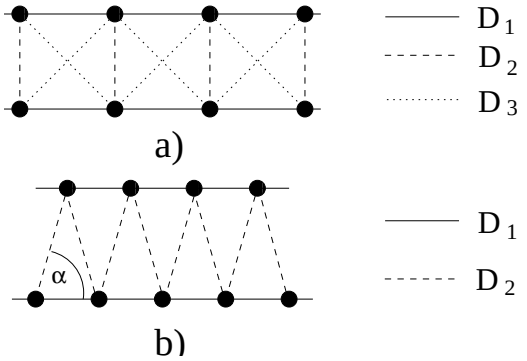

FIG. 12: Square (a) and triangular (b) ladder lattices. Different types of lines represent different spring constants. In the triangular ladder all springs of force constant D_2 have the same unstrained length.

Acknowledgments

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