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# Oscillation processes during acoustic wave propagation in monolayer phosphorene

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Acoustic waves can arise in crystals as a result of slow continuous longitudinal compression and are an effective way to transfer energy over long distances deep into the crystal without significantly changing its properties. Acoustic wave propagation in two-dimensional (2D) materials is much less studied than in 3D crystals. Molecular dynamics simulations are used to analyze acoustic dynamics in single-layer phosphorene. We analyze the mechanisms of wave propagation in different crystallographic directions and the effect on the wave properties due to the high lattice anisotropy of phosphorene. As part of the analysis, we study the vibrations of the atoms through which the acoustic wave travels in both inert and moving coordinate systems. This enables us to analyze in detail the wave propagation process and the dynamics of the vibrations of the atoms arising after the wave passes through them. In general, our results contribute to the understanding of the nonlinear dynamics of localized excitations in two-dimensional materials.

**Keywords:** 2D materials, phosphorene, extreme impacts, acoustic waves, molecular dynamics, longitudinal compression.

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## Introduction

The separation of graphene from a three-dimensional substance — graphite [1] — became an important breakthrough in scientific research and opened a new direction in the synthesis and study of various two-dimensional materials. Progress in technologies for separation and processing of layered materials has led to the possibility of creation of new single-layer materials, including phosphorene — a two-dimensional layer of black phosphorus [2]. Despite the fact that black phosphorene is the most stable form of phosphorus, it became possible to synthesize only many decades after the discovery of the chemical element phosphorus itself. Graphene and phosphorene are monolayer crystal structures consisting of the same atoms. The discovery of phosphorene has opened up new perspectives for study of this material and its potential applications in various fields.

Studies focusing on the electronic properties of a monolayer or several layers of black phosphorus were conducted in 2014 [3]. These studies have shown that phosphorene has semiconductor conductivity and is characterized by high mobility of charge carriers. This means that phosphorene has significant potential for the development of high-efficiency and high-performance electronic devices. The prospects of using phosphorene in various technological applications were also confirmed. Its ability to absorb light better than other two-dimensional materials such as graphene makes it potentially useful for a variety of electronic applications, including photodetectors and LEDs.

Phosphorene as a relatively new object of research attracts a lot of attention from the scientific community. A significant number of review articles have been published on this two-dimensional material in recent years. These reviews describe in detail its properties, production methods and various devices created on the basis of phosphorene [4]. They provide information about its properties and the potential use of phosphorene in various fields.

One of the important aspects of phosphorene is that it has unique thermal characteristics that differ significantly from the properties of macroscale three-dimensional black phosphorus [5]. It turned out that phosphorene has high thermal stability, which means that it retains its properties even at very high temperatures without degradation of its crystal structure. This opens up new prospects for its use in various thermal applications where high stability and efficiency are required.

Also, apparently phosphorene can become an effective thermoelectric material with high electrical conductivity and low thermal conductivity [6]. Thermoelectric materials have the ability to convert thermal energy into electrical energy. Phosphorene due to its properties is a promising candidate for the creation of thermoelectric devices, for example, thermogenerators. Moreover, phosphorene can serve as a catalyst due to its high surface activity and the ability to change its structure during the reaction process. This opens up new possibilities for various chemical processes and industrial productions where efficient and flexible catalysis is required.

The molecular dynamics method is a highly effective tool for studying the transformation of the structure of two-dimensional materials. It allows detailed modeling of various processes in materials at the atomic level, opening up new opportunities for understanding their behavior and properties. For example, the processes of peeling and sliding of graphene nanoribbons can be studied using the molecular dynamics method, which is an important aspect for understanding and controlling structural changes in such materials [7]. This method also makes it possible to simulate thermally and mechanically induced pulsation in two-dimensional materials [8]. Another example is the possibility of studying surface pulsations and twistons, which contributes to a deeper understanding of the interaction of the material with the environment and its reaction to external impacts [9]. It is also possible to study the excitation and motion of solitons, shock waves in graphene and other two-dimensional materials through modeling.

The molecular dynamics method is a useful tool for studying the transfer of heat, energy, and mass in two-dimensional materials. It allows for studying various aspects of thermal dynamics, including ballistic heat transfer and energy equalization in a two-dimensional harmonic graphene lattice, which is important for understanding thermal conductivity and other energy properties of two-dimensional materials and may be useful for the development of new thermoelectric devices [10]. In addition, the molecular dynamics method makes it possible to study the effects of localized shock loads and vibrations in two-dimensional materials, including spatially localized vibrational modes such as discrete breezers. The latter may be important in analyzing the mechanical properties and stability of materials [11]. The behavior of two-dimensional materials under extreme conditions such as high temperatures and high pressures can be also modelled using the molecular dynamics method which allows for a deeper understanding of the role of nonlinear energy channels in extreme conditions [12].

Two-dimensional materials used in various devices are often subjected to extreme dynamic loads. The study of energy transfer mechanisms in such materials, including nonlinear effects, plays an important role in understanding their properties and behavior under high-speed deformation conditions [10]. Scientific studies confirm that the behavior of two-dimensional materials under high-speed strain differs significantly from their behavior at low strain rates [11]. This is of particular importance when considering materials such as carbon nanotubes, which, when exposed to a shock wave, experience significantly more damage compared to static compression at the same pressure value [12].

However, there are two-dimensional materials that have special properties that can cope with high-speed deformation without destruction. For example, graphene has the potential for the application as a material capable of absorbing shock waves and mitigating their effect, as well as a layer reflecting and attenuating shock waves [13,14]. These studies suggest the prospects of using two-dimensional materials in the field of protection from shock waves and other high-energy dynamic loads.

Phosphorene, unlike graphene and boron nitride, has a more complex spatial structure and consists of two subatomic layers, which gives phosphorene different properties compared to graphene. Phosphorene is a highly anisotropic material, i.e. its properties significantly depend on its direction. For example, the Young's modulus of phosphorene in the „zigzag" direction ranges from 90 to 166 GPa, while it ranges from 40 to 44 GPa in the „chair" direction [15]. Studies show that phosphorene, subjected to short-term high-intensity exposure, can exhibit similar with graphene and boron nitride properties of solitonic compression waves [16,17]. Such waves are excited during short-term localized high-intensity deformation of the material.

The objectives of this study are to analyze the dynamics of atoms during the excitation and propagation of acoustic waves occurring in a material during slow longitudinal compression, to identify differences in the vibrational dynamics of atoms depending on the propagation range of the acoustic wave, the impact of the propagation direction and the compression rate of the crystal lattice on it.

## 1. Research methods

Phosphorene is a material that is a single-layer crystal consisting of phosphorus atoms. Visually, it is a two-dimensional material with a complex spatial topology, which is schematically shown in Fig. 1. Two-level structure is one of the characteristic features of phosphorene. Each phosphorene translational cell consists of four phosphorus atoms, which are distributed over two parallel levels in the plane $XY$.

Phosphorus atoms are designated as $P_1$ in the upper level of phosphorene, whereas in the lower level they are designated as $P_2$. This separation into upper and lower

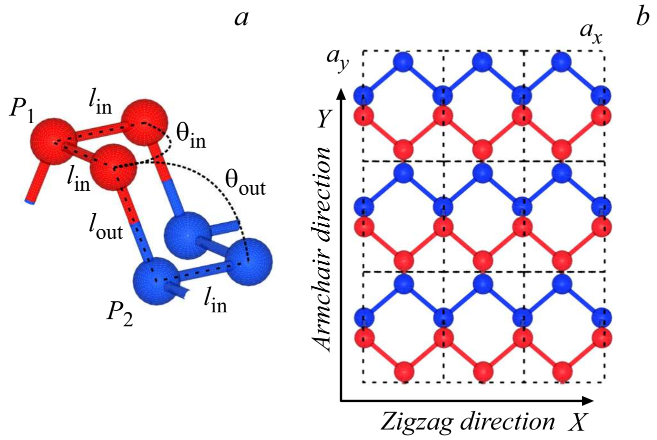


**Figure 1.** Schematic representation of the phosphorene crystal lattice. *a* — image of one translational cell in perspective, *b* — top view of $3 \times 3$ translational phosphorene cells. Each cell is highlighted with a dashed line.

levels creates a special structure with two types of valence bonds. One of them, named $l_{\text{in}}$, is located only in the same level (either the upper $P_1$ or the lower $P_2$) and is called an internal bond. Another bond, called $l_{\text{out}}$, connects atoms at different levels $P_1$ and $P_2$ and is called an external bond, as shown in Fig. 1, *a*. Also, in turn, such a topology allows defining two different types of valence bond angles, denoted as $\theta_{\text{in}}$ (inner corner) and $\theta_{\text{out}}$ (outer corner) accordingly.

Studies in Ref. [18] allowed for determining a fairly effective approach to describing the interaction of phosphorene atoms using the Stillinger-Weber potential (SW). This potential was previously successfully used to model atomic interactions in silicon [19]. The speed of sound and the dispersion of phonons obtained as a result of basic calculations are well reproduced when describing the interaction of phosphorus atoms with such a potential, the crystal structure. The SW potential consists of two parts: a two-particle term describing the bond lengths and a three-particle term describing the bond angles.

The values of the potential parameters are selected in accordance with [18]. The following lattice parameters are obtained when using these parameter values: the length of the internal bond is $l_{\text{in}} = 2.21$ Å, and the length of the bond between atoms from the upper and lower levels is $l_{\text{out}} = 2.258$ Å. The phosphorene lattice parameters have the values $a_{\text{x}} = 3.284$ Å and $a_{\text{y}} = 4.59$ Å. The bond angles are $\theta_{\text{in}} = 95.999°$ and $\theta_{\text{out}} = 104.0°$. The equilibrium energy per atom is $\Delta E = 3.48$ eV. It should be noted that all these values are very close to the results obtained by the calculations of the first principles in Ref. [20].

The widely used LAMMPS software package is used for molecular dynamic modeling of the interaction of phosphorene atoms [21]. The integration of the equations of motion of atoms is performed using the Verlet method with a time step of 0.2 fs. The boundary conditions are periodic in all three directions. However, a vacuum layer with a thickness of 20 Åin the direction of $Z$ was introduced to exclude the interaction of the considered phosphorene sheet with its periodic images.

The phosphorene crystal lattice used in the simulation consists of 192,000 atoms. Its dimensions depend on the direction of compression of the lattice: for the case of compression along the direction „zigzag“ the lattice has dimensions $367.18 \times 19.7 \times 2.0$ nm, and for compression along the direction „chair“ the dimensions are $27.54 \times 266.7 \times 2.0$ nm. The phosphorene crystal lattice undergoes continuous compression in the modeling process using a piston that moves at a constant speed $u$ along one of the crystallographic directions. This compression results in intense heating of the grating and the excitation of acoustic or shock waves, depending on the speed of the piston. It is important to note that the stochastic effects of the crystal temperature are not taken into account in this work, therefore it is assumed that the initial lattice temperature is 0,K. This means that all atoms are in their equilibrium positions until they are exposed to acoustic or shock waves excited in the crystal due to lattice compression.

## 2. Results

An acoustic wave is excited in crystal lattice when the crystal lattice is compressed at a speed of less than the speed of sound in phosphorene propagating along one of the crystallographic directions such as „of the chair“ or „of the zigzag“. The lattice is strongly heated at the boundary of the acoustic wave front as a result of such an action. At the same time, the compression of the lattice is much faster than the speed of the piston, namely, it has the speed of sound in phosphorene. The mechanism of such displacement relative to the equilibrium position employs an acoustic wave. The wave rests in its equilibrium position until it reaches the atom located along one of the crystallographic directions along which the wave propagates. After an acoustic wave reaches the atom and passes through it, the atom begins to shift at the speed of the piston, like the rest of the lattice, through which the wave has already passed. This process is clearly visible when considering the dynamics of the position of atoms, shown in Fig. 2 for the case of two velocities $u = 0.1$ (*a,c*) and 0.5 m/s (*b,d*) when the wave propagates along the „chair“ (*a,b*) and „zigzag“ (*c,d*) direction.

The graphs show the temporal dynamics of the coordinates $y$ (for movement along the „zigzag“ direction) or $x$ (for movement along the „chair“ direction) of every tenth atom in the atomic row located along one of the crystallographic directions of phosphorene. They are highlighted with lines of different colors. It can be noted that the distance between atoms in the case of propagation along the „chair“ is significantly less than in the case of propagation along the „zigzag“. This is attributable to the structure of phosphorene, in which the projection of the interatomic distance along $Y$ („chair“) or $X$ („zigzag“)

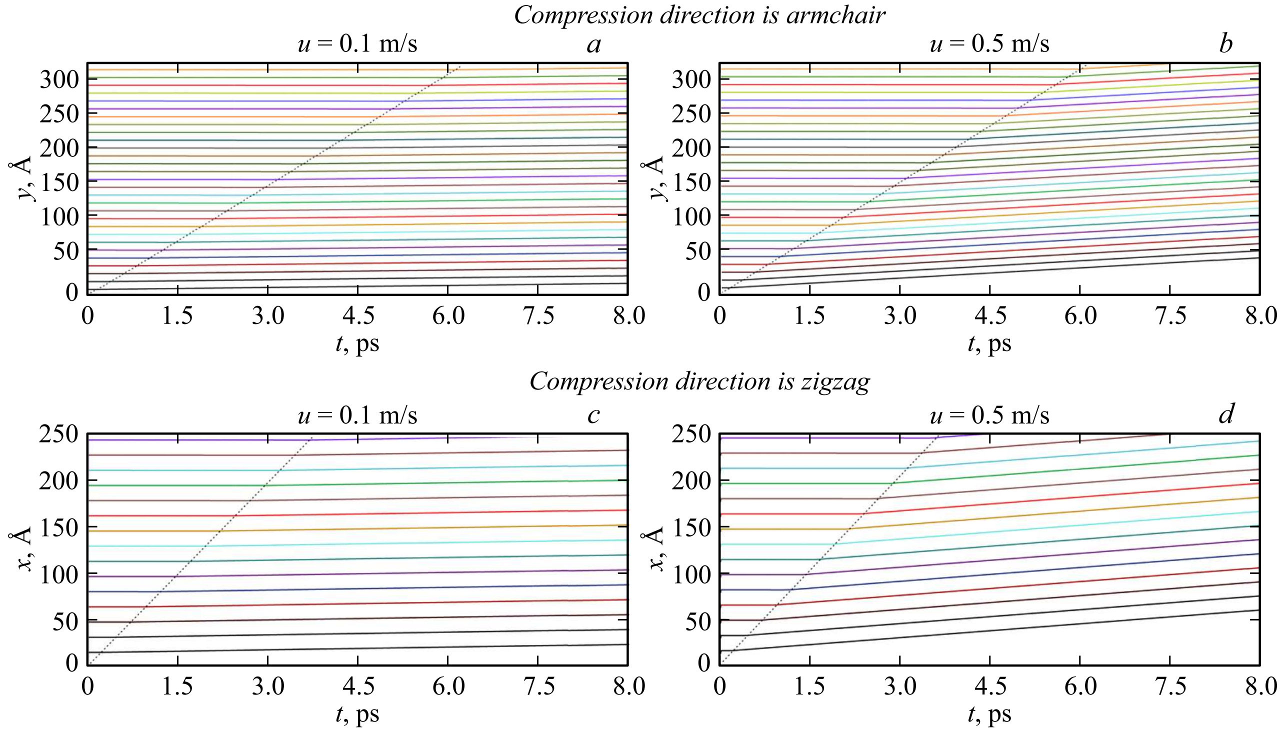


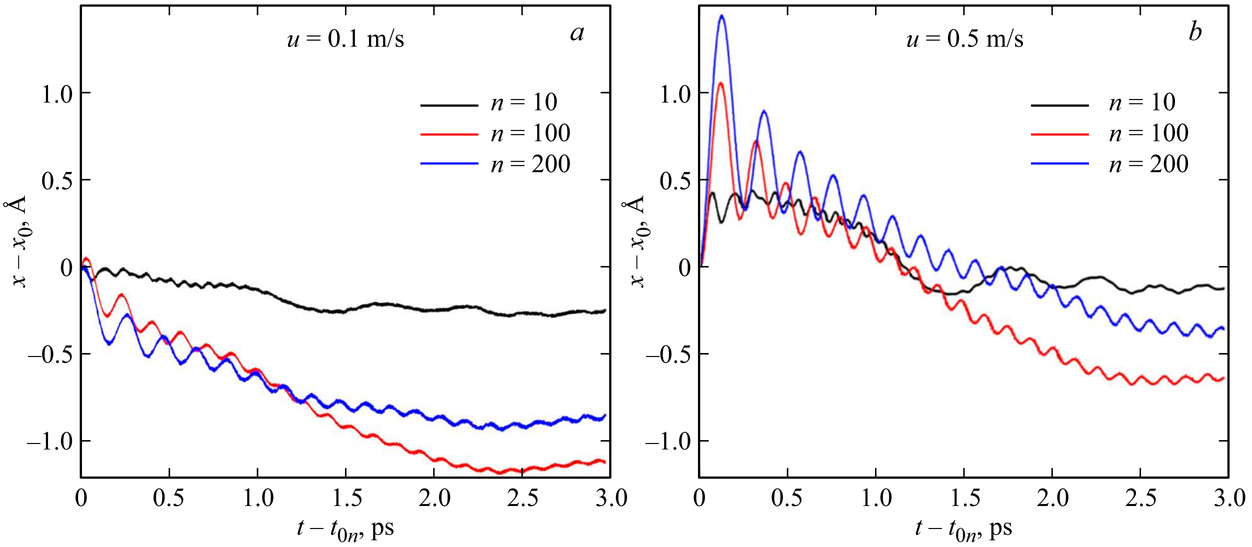
**Figure 2.** Dynamics of atomic coordinates during propagation of an acoustic wave excited by a piston compressing the crystal lattice at a speed of $u = 0.1$ m/s (*a,c*) and $u = 0.5$ m/s (*b,c*) in the „chair“ (*a,b*) and „zigzag“ (*c,d*) direction. The colored lines show the curves of change in the coordinates of each 10th atom of the series along the crystallographic direction. The dotted line marks the moment of passage through the atom of the wave.

differs significantly (Fig. 1, *b*). The graph clearly shows that the wave was at rest and did not move (horizontal line, without tilt in Fig. 2) until it reached the atom despite the compression of the lattice. However, after the wave passes through the atom, it moves at a speed close to the speed of the piston. The difference in piston speeds is clearly visible when comparing graphs (at $u = 0.5$ m/s the angle of inclination is significantly higher than at $u = 0.1$ m/s). A fracture appears on graphs at the moment of passing through the atoms of the wave, corresponding to the beginning of the displacement of atoms. At this point, it is possible to determine the propagation velocity of an acoustic wave. These time points are connected by a line, according to the tangent of the angle of inclination of which the wave velocity is calculated. It can be noted that the speeds of the wave are the same despite the significantly different speeds of the piston in the same crystallographic direction. This velocity for acoustic waves is determined by the speed of sound in the crystal and does not depend on the piston velocity. It should be noted that the wave velocity in the „chair“ direction is significantly lower than along the „zigzag“ direction. This is attributable to the pronounced anisotropy of phosphorene. If we calculate the velocity of the wave according to the graph, it turns out that it is equal to the value of the speed of sound indicated in the literature: 4.6 km/s for movement along the „chair“ and 8 km/s for propagation along the „zigzag“.

The question arises, how exactly does the wave pass through the atoms? Do the atoms only begin to shift with the speed of the piston, or is there also an oscillatory dynamics? And does such dynamics change as the acoustic wave propagates through time and space? The study of these problems is complicated by the fact that atoms rest before the wave, and immediately after the passage of the wave they begin to shift. Consequently, the oscillatory dynamics becomes invisible against the background of displacement. An algorithm has been developed that allows considering the dynamics of the position of an atom in a moving coordinate system, which compensates for the effect of displacement and allows for a more detailed consideration of behavior of atoms.

The dependences of the coordinates ($X$ or $Y$ depending on the direction of wave propagation) of atoms relative to their equilibrium position in a moving coordinate system are shown in Fig. 3 for $n = 10$, 100, 200 atoms, where $n$ is the number of the atom in the atomic series. These graphs show the process of the wave propagation through the atom, as well as the subsequent dissipation of the received energy in the form of phonons. The atom receives a displacement relative to the equilibrium position when a wave propagates throughs it, after which the atom begins to oscillate with a decaying amplitude. It can be noticed that the vibrations of atoms are stronger the farther away the wave is. This is attributable to the fact that the tensions in lattice are

Compression direction is armchair



Compression direction is zigzag

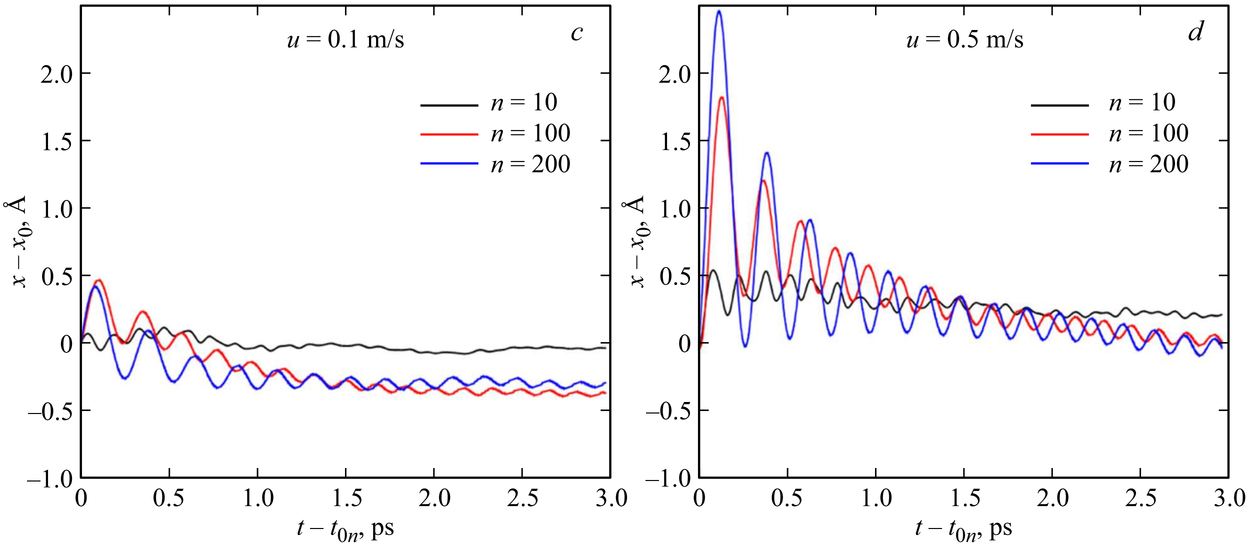


**Figure 3.** Dynamics of the coordinates of atoms numbered $n = 10$, 100 and 200 in the atomic series in a moving coordinate system starting from the moment of passage through the atom of the wave $t_n$ during the propagation of an acoustic wave excited by a piston compressing the crystal lattice at a speed of $u = 0.1$ m/s (*a,c*) and 0.5 m/s (*b,d*) in the „chair" (*a,b*) and „zigzag" (*c,d*) direction.

increasing due to the continuous compression of the lattice and the wave energy is also monotonously increasing. As a result, the wave increasingly deflects the atom from its equilibrium position. At the same time, the frequency of residual vibrations of the position of atoms, on the contrary, decreases with the propagation of the wave. The highest frequency of vibrations of the atomic position is observed at the beginning of the lattice, and then it becomes less and less. This can be explained by the fact that the velocity of wave propagation significantly exceeds the speed of the piston and the atoms are less affected by compression at a distance from the beginning of the lattice, therefore, the dissipation of the received energy decreases, as evidenced by a decrease of the frequency of vibrations. It is also worth noting that the frequency of vibrations of atoms is noticeably lower when the acoustic wave propagates in the direction „zigzag" (by about 25%). Interestingly, the acoustic wave slightly slows down as it propagates during the propagation of the wave along the „chair"İThis is evidenced by the time-decreasing value of the position of the atom in Figure 3 (in a moving coordinate system) (it becomes negative), and this deviation increases with the propagation of the wave. For the case of propagation along a zigzag, no such effect is observed.

## Conclusion

A study of the continuous compression of a monolayer phosphorene lattice along one of the crystallographic directions showed that an acoustic wave is excited in the lattice at subsonic speeds of the compressing piston. It was found that the velocity of the acoustic wave does not depend on the speed of the piston and is determined by the speed of sound in the crystal. The velocities of acoustic waves differ almost 2 times depending on the direction of propagation due to the high anisotropy of phosphorene, namely 4.6km/s in the „chair“ direction and 8 km/s in the „zigzag“ direction. It was also found that it is impossible to use the SW potential with the parameters for phosphorene [18] at high piston speed, since the lattice collapses, some atoms near the piston receive enormous kinetic energy which results in the quick loss of stability of the lattice.

The dynamics of atoms through which an acoustic wave propagates was studied. For this purpose, the atom dynamics was considered in a moving coordinate system with the speed of the piston, since the atom begins to shift at this speed in the direction of movement of the piston after the propagation of the wave. At the moment when a wave passes through the atom, it receives an additional impulse and deviates from its initial position. Then the atom relaxes back, then forward, and so on, making phononic vibrations. The frequency of these oscillations characterizes the dissipation of the received energy into the lattice — the higher is the oscillation frequency, the higher is the energy dissipation. In phosphorene, the maximum frequency of phonon oscillations is observed at the initial stage of wave propagation, and it decreases with its further propagation. It should also be noted that due to continuous compression, the acoustic wave constantly receives additional energy and the energy dissipation for residual vibrations of atoms is fully compensated.

In the future, it is planned to modify the potential with a more correct description of the compressive part of the potential so that it is possible to study the dynamics of shock waves.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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