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Mechanical stability of simple planar lattices

Krystyna Żabińska
Laboratory of Physics, Academy of Economics, Rynek Gł. 34, 31-010 Kraków, Poland

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Elastic constants of simple two-dimensional structures, monatomic square, monatomic hexagonal, and diatomic square, have been calculated with different pairwise atom-atom potentials of the general form $V(r)=-A/r^n+B/r^m$, with different A, B, n, and m parameters. The general conditions for the potential parameters have been found to assure stability of the lattices. It is shown that the monatomic square structure can never be stable with the parameters used. On the other hand, the hexagonal monatomic lattice is always stable. Only in the case of the diatomic square lattice does the stability depend on the actual values of the potential parameters. These results explain why in the majority of atomic crystals the (001) surfaces are reconstructed, rough, or stepped, and not planar square.

I. INTRODUCTION

The simple planar lattices are interesting for theoretical studies for a few reasons. The first is that the two-dimensional structures appear in nature as surfaces[1-3] or interfaces.[4] Sometimes the planar lattices can also be considered to illustrate certain properties of real three-dimensional crystals. A planar model proposed by Pick[5] has thoroughly been examined from this point of view.[6-12] In the latter model two kinds of atoms form the diatomic square structure, in which each atom of one kind is located at the center of the square formed by the atoms of the other kind. The lattice has been proved to be stable whenever the short-range repulsion expressed, e.g., by the Born-Mayer formula, is compensated by the Coulomb electrostatic forces coming from the charges of opposite signs placed at both kinds of atoms. It has turned out that such a lattice becomes mechanically unstable when the charge is less than a certain critical value.[12]

An interesting question now is whether it is at all possible to construct the above-described diatomic square structure using only the short-range atom-atom potentials: the Buckingham 6-exp potential

$$V_B(r)=A\exp(-Br)-C/r^6$$

or the Lennard-Jones

$$V_{\mathrm{LJ}}(r)=A/r^{12}-C/r^6 .$$

The attempts made until now with a wide range of the parameters of both potentials have never given any stable square structure.[12]

The aim of the present paper is to find the atom-atom potentials that are able to make stable some simple planar lattices. The lattices considered here are hexagonal, monatomic square, and diatomic square. These are the structures most often inferred by the unreconstructed surfaces of crystals. The examined potentials have the form of

$$V(r)=-A/r^n+B/r^m$$

with different A, B, n, and m. The values $n=6$ and $m=12$ are most often used in the calculations for bulk materials. Some other values of n and m are used in packing-analysis calculations for crystals.[13] The point, however, is that when the square structure constitutes a surface of the crystal, the effective atom-atom interactions mediated by the underlying lattice may well be very different from those among the bulk atoms.

The relations between elastic constants and the second derivatives of the potential function for the hexagonal lattice, the monatomic square lattice, and the diatomic square lattice are given in Sec. II. The mechanical stability of these lattices for the various potential functions is discussed in Sec. III. The obtained results can cast light on the experimental observations of the surfaces of crystals. The short discussion of this problem is given in Sec. IV.

II. ELASTIC CONSTANTS IN A SHORT-RANGE INTERACTION MODEL

Let us consider a perfect planar lattice with atoms (particles) which interact by central forces. If all the atoms of the structure are placed at centrosymmetric sites, the potential-energy density may be written in the harmonic approximation as only dependent on the macroscopic strain components s_σ, $\sigma=1,2,6$:

$$u=\tfrac{1}{2}\sum_{\sigma,\rho} c_{\sigma\rho}s_\sigma s_\rho , \tag{1}$$

where $c_{\sigma\rho}$ are the elastic constants of the crystal.[14] The range of the Voigt indices σ and ρ in the two-dimensional lattice is $xx=1$, $yy=2$, $xy=yx=6$.

The elastic constants $c_{\sigma\rho}$ depend on the interactions among the atoms of the crystal in the following way:

$$\begin{aligned} c_{\sigma\rho}&=(\alpha\beta\gamma\lambda)\\ &=\frac{2}{v_a}\sum_{l'}\sum_{\kappa}\sum_{\kappa'}[\psi''x_\alpha x_\beta x_\gamma x_\lambda]_{\mathbf{x}\left(\begin{smallmatrix} l' \\ \kappa,\kappa'\end{smallmatrix}\right)} , \end{aligned} \tag{2}$$

where v_a is the volume of the unit cell. The summation goes over all the unit cells and over all the types of atoms (κ,κ') within each cell. $\psi(r^2)$ is a function related with the pairwise central atom-atom potential $V(r)$: $V(r)=\psi(r^2)$, where r is the distance between atoms $r=(x_1^2+x_2^2)^{1/2}$. The subscript

$$\mathbf{x}\begin{bmatrix} l' \\ \kappa,\kappa' \end{bmatrix}$$

in the expression $[\psi'' x_\alpha x_\beta x_\gamma x_\lambda]$ indicates that the second derivatives

$$\psi''(r^2)=\frac{\partial^2\psi(r^2)}{\partial(r^2)^2}$$

are taken for

$$r^2\equiv|\mathbf{r}|^2=\left|\mathbf{x}\begin{bmatrix} l' \\ \kappa' \end{bmatrix}-\mathbf{x}\begin{bmatrix} 0 \\ \kappa \end{bmatrix}\right|^2$$

$$=|\mathbf{x}(l')+\mathbf{x}(\kappa')-\mathbf{x}(\kappa)|^2 . \tag{3}$$

The elastic constants given by Eq. (2) are completely symmetric in all four tensor indices. Consequently, there are only five independent elastic constants in this case, the ones c_{12} and c_{66} obeying the Cauchy relation

$$c_{12}=c_{66} . \tag{4}$$

Thus, the elastic constants in Eq. (1) may be arranged in the following matrix:

$$D=\begin{bmatrix} c_{11} & c_{12} & c_{16} \\ c_{12} & c_{22} & c_{26} \\ c_{16} & c_{26} & c_{12} \end{bmatrix} . \tag{5}$$

A further reduction in the number of independent elastic constants is connected with the symmetry of the planar lattice. Figure 1 shows three types of two-dimensional lattices discussed in the paper. A lattice constant a is depicted in Fig. 1 for each type of the lattice.

A. Monatomic square lattice

In the square lattice of symmetry 4 mm, only two elastic constants c_{11} and c_{12} are independent. The other being $c_{22}=c_{11}$, $c_{16}=c_{26}=0$, and, owing to the Cauchy relation, $c_{66}=c_{12}$.

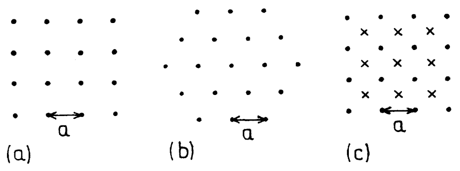

FIG. 1. Simple planar lattices treated in the article: (a) monatomic square, (b) monatomic hexagonal, (c) diatomic square. The lattice constant a is depicted for all the above structures.

The lattice points in the square lattice [Fig. 1(a)] can be expressed as

$$l_1\mathbf{a}_1+l_2\mathbf{a}_2 , \tag{6}$$

where l_1,l_2 are integers and $\mathbf{a}_1,\mathbf{a}_2$ are basic lattice vectors. If the Cartesian axes are chosen parallel to the vectors $\mathbf{a}_1,\mathbf{a}_2$, we find from Eq. (2) that

$$c_{11}=\frac{2a^4}{v_a}\sum_l l_1^4\psi''[a^2(l_1^2+l_2^2)] \tag{7}$$

and

$$c_{66}=c_{12}=\frac{2a^4}{v_a}\sum_l l_1^2 l_2^2\psi''[a^2(l_1^2+l_2^2)] . \tag{8}$$

For a lattice to be stable, the energy density [Eq. (1)] must be a positive definite quadratic form. This condition is assured by the positive values of the all principal minors. For the square lattice, the principal minors are

$$c_{11},\quad c_{11}^2-c_{12}^2,\quad c_{12}(c_{11}^2-c_{12}^2) . \tag{9}$$

The following three conditions need to be fulfilled to assure the mechanical stability of the lattice:

$$c_{11}>0,\quad c_{12}>0,\quad c_{11}-c_{12}>0 . \tag{10}$$

It follows from Eqs. (7) and (8) that the first term in the expansion for c_{11} is equal to the analogous term for $c_{11}-c_{12}$ and they are both proportional to $\psi''(a^2)$. The value of c_{12} calculated from Eq. (8) is

$$c_{12}=\frac{2a^4}{v_a}[4\psi''(2a^2)+32\psi''(5a^2)+64\psi''(8a^2)+\cdots] . \tag{11}$$

To obtain Eq. (11), the interactions between the nearest neighbors to the fifth coordination sphere have been taken into account. The first term in Eq. (11) is proportional to the second derivative $\psi''(2a^2)$ of the potential function for the second-nearest neighbors. The monatomic square lattice, then, can be stable for short-range potentials if this term is positive. If ψ'' turns out to be negative for all but the first-nearest neighbors, the square lattice will be unstable. This is, in fact, most likely to be the case, because the inflection point of the function $\psi''(r^2)$ usually falls at a distance r between the first and the second coordination spheres.

B. Hexagonal lattice

It follows from the symmetry of the hexagonal lattice that

$$c_{66}=\tfrac{1}{2}(c_{11}-c_{12}) . \tag{12}$$

Taking the Cauchy relation [Eq. (2)] into account, one obtains

$$c_{66}=c_{12}=\tfrac{1}{3}c_{11} . \tag{13}$$

There is only one independent elastic constant c_{11} for the hexagonal lattice.

The basic vectors of the hexagonal lattice [Fig. 1(b)] can be chosen as

$$\mathbf{a}_1=(a,0),\quad \mathbf{a}_2=\left[\frac{1}{2}a,\frac{\sqrt{3}}{2}a\right] . \tag{14}$$

The summation in Eq. (7) runs, in this case, over the following lattice points:

$$\mathbf{x}(l)=\left[l_1+\tfrac{1}{2}l_2,\frac{\sqrt{3}}{2}l_2\right]a . \tag{15}$$

The elastic constant c_{11} obtained with the use of Eq. (7) reads (for the interactions up to the fifth-nearest neighbors)

$$c_{11}=\frac{a^4}{v_a}\frac{9}{2}[\psi''(a^2)+9\psi''(3a^2)+16\psi''(4a^2)+98\psi''(7a^2)+81\psi''(9a^2)+\cdots] . \tag{16}$$

For the lattice to be stable, the value of c_{11} must be positive. Since the first term in Eq. (16) is proportional to the second derivative of the potential function ψ for the first-nearest neighbors, the hexagonal lattice is most likely to be stable. It follows from the fact that the distance between the nearest neighbors in a lattice in equilibrium generally falls very close to a minimum of the atom-atom potential function $\psi(r^2)$. The lattice atoms (particles) interact predominantly with their nearest neighbors for the short-range potentials.

Another reason for the stability of the hexagonal lattice is the number of the first-nearest neighbors. The most stable structure is the one in which there are as many as possible first neighbors giving the decisive contribution to the total energy. There are six of these kinds of neighbors for the hexagonal lattice and only four in the case of the square lattice.

C. Diatomic square lattice

The diatomic square lattice is presented in Fig. 1(c). The symmetry of the structure restrains the number of the independent elastic constants to c_{11}, c_{12}, and c_{66}. The Cauchy relation [Eq. (4)] reduces them to c_{11} and c_{12}. There are two kinds of atoms in the unit cell. The summation in Eq. (7) runs in the lattice over the following points:

$$\mathbf{x}_1(l)=(l_1,l_2)a \tag{17}$$

for the interactions of two identical atoms and

$$\mathbf{x}_2(l)=(l_1+\tfrac{1}{2},l_2+\tfrac{1}{2})a \tag{18}$$

for the interactions of two different atoms.

According to Eqs. (7) and (8), the term $\psi''(\frac{1}{2}a^2)$ enters the expressions for the elastic constants c_{11} and c_{12} with the same coefficients. The only condition for the crystal to be stable then is

$$c_{11}-c_{12}>0 . \tag{19}$$

Taking into account the interactions up to the fifth-nearest neighbors, one obtains

$$c_{11}-c_{12}=\frac{2a^4}{v_a}2[\psi''(a^2)+4\psi''(\tfrac{5}{2}a^2)+16\psi''(4a^2)+\cdots] . \tag{20}$$

Therefore, as in the case of the monatomic square lattice, the stability of the diatomic one is conditioned by the positive sign of the second derivative of the function ψ taken at the distance of the second-nearest neighbors.

III. MECHANICAL STABILITY OF SIMPLE PLANAR LATTICES

A. Monatomic square lattice

Let us assume the potential function of the form

$$V(r)=-\frac{A}{r^n}+\frac{B}{r^m} \tag{21}$$

with $n<m$.

The first and the second term in Eq. (21) correspond to the attractive and repulsive forces, respectively. The potential-energy density for the monatomic square lattice is given by

$$u=\tfrac{1}{2}4\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}\left[-\frac{A}{[a(l^2+k^2)^{1/2}]^n}+\frac{B}{[a(l^2+k^2)^{1/2}]^m}\right] . \tag{22}$$

The value of the lattice constant a is taken from the minimization of the energy [Eq. (22)]. The condition

$$\frac{\partial u}{\partial a}=0 \tag{23}$$

leads to the following expression for a:

$$a^{m-n}=\frac{Bm}{An}\frac{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+k^2)^{-m/2}}{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+k^2)^{-n/2}} . \tag{24}$$

Putting $x=r^2$, one can formally rewrite the potential given by Eq. (21) in the following form:

$$\psi''(x)=-\frac{A}{x^{n/2}}+\frac{B}{x^{m/2}} . \tag{25}$$

The second derivative of the above potential function reads

$$\psi''(x)=-\frac{n(n+2)A}{4(x^{n+4})^{1/2}}+\frac{m(m+2)B}{4(x^{m+4})^{1/2}} . \tag{26}$$

Inserting this expression into Eq. (8), one obtains the condition of the mechanical stability of the square monatomic lattice

$$c_{12}=\frac{2a^4}{v_a}4\sum_{l=1}^{\infty}\sum_{k=1}^{\infty}l^2k^2\left[-\frac{n(n+2)A}{4[a^2(l^2+k^2)]^{(n+4)/2}}+\frac{m(m+2)B}{4[a^2(l^2+k^2)]^{(m+4)/2}}\right]>0 . \tag{27}$$

Equation (24) allows us to rewrite the inequality (27) as follows:

$$\frac{(m+2)\sum_{l=1}^{\infty}\sum_{k=1}^{\infty} l^2k^2(l^2+k^2)^{-(m+4)/2}}{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+k^2)^{-m/2}} > \frac{(n+2)\sum_{l=1}^{\infty}\sum_{k=1}^{\infty} l^2k^2(l^2+k^2)^{-(n+4)/2}}{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+k^2)^{-n/2}} \, . \qquad (28)$$

One can see that expression (28) is independent of the potential parameters A and B. It only depends on the exponents n and m in the potential function [Eq. (21)]. In practical calculations, the interactions are neglected beyond a certain distance, especially if the exponents n and m are large enough. In such an approximation the values of the sums in formula (28) will also depend on the number N of the coordination spheres taken in by the assumed range of interactions. The explicit form of the inequality (28) allows one to rewrite it as follows:

$$f(m,N) > f(n,N) \qquad (29)$$

since both sides of it are expressed by the same functions with only different parameters n or m.

Several functions $f(n,N)$ are shown in Fig. 2 for different exponents n and different numbers N. For a large value of n ($n > 12$) the function $f(n,N)$ is practically independent of the number N. It is then enough to consider the interactions between the first- and the second-nearest neighbors only, i.e., $N=2$. [If $N=1$ then $f(n,1)=0$ for any value of n.] Several values of $f(n)$ for $n > 12$ are shown in Fig. 3.

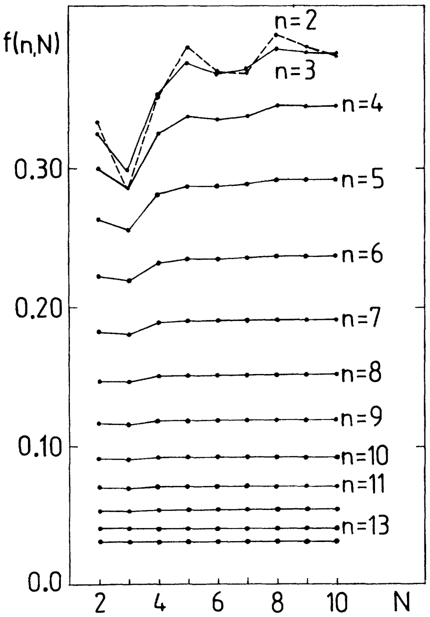

FIG. 2. Quantity $f(n,N)$ [see Eq. (28)] for a monatomic square lattice as a function of the maximal range of interactions N and calculated for several values of exponent n. Lines are given to guide the eyes.

For $n \geq 2$ and $m \geq 4$, $f(m,N) \leq f(n,N)$ so that the monatomic square lattice is always unstable (see Figs. 2 and 3) whatever the parameters in the potential might be.

Inequality (29) is fulfilled for $n=2$ and $m=3$ for certain numbers N as it follows from Fig. 2. It is, therefore, possible to obtain the stable monatomic square lattice in very specific cases of $N=3$, 4, 7, or 10. Otherwise, the lattice is also unstable.

B. Hexagonal lattice

Let us consider the stability of the hexagonal structure for the potential function given by Eq. (21). The potential-energy density for this lattice [see Fig. 1(b)] reads

$$u = -\frac{A}{a^n}\left[\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+kl+k^2)^{-n/2} + \sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2-kl+k^2)^{-n/2})\right] + \frac{B}{a^m}\left[\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+kl+k^2)^{-m/2} + \sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2-kl+k^2)^{-m/2}\right] . \qquad (30)$$

The value of the lattice constant a is then [see Eq. (23)]

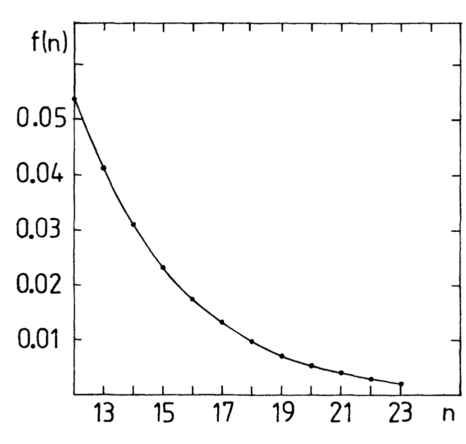

FIG. 3. The same as in Fig. 2 but for $n > 12$ when the quantity $f(n,N)$ becomes N independent.

$$a^{m-n}=\frac{mB}{nA}\,\frac{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+kl+k^2)^{-m/2}+\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2-kl+k^2)^{-m/2}}{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2+kl+k^2)^{-n/2}+\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(l^2-kl+k^2)^{-n/2}}\ . \tag{31}$$

The condition for stability of the hexagonal lattice reads

$$c_{11}=\frac{2}{v_a}a^4\sum_{l=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}(l+\tfrac{1}{2}k)^4\psi''\left\{a^2\left[(l+\tfrac{1}{2}k)^2+\left[\frac{\sqrt{3}}{2}k\right]^2\right]\right\}>0\ . \tag{32}$$

Putting Eqs. (26) and (31) into Eq. (32) and limiting the interactions to the Nth coordination sphere, one gets the stability condition for the hexagonal lattice

$$f_h(m,N)>f_h(n,N)\ , \tag{33}$$

where

$$f_h(\nu,N)=\frac{(\nu+2)\left[(1+\frac{1}{16})\sum_{l=1}^{L}l^{-\nu}+\sum_{l=1}^{L}\sum_{k=1}^{K}(l+\frac{1}{2}k)^4(l^2+kl+k^2)^{-(\nu+4)/2}\right]}{\sum_{l=0}^{L}\sum_{k=1}^{K}(l^2+kl+k^2)^{-\nu/2}+\sum_{l=0}^{L}\sum_{k=1}^{K}(l^2-kl+k^2)^{-\nu/2}}$$
$$+\frac{(\nu+2)\sum_{l=1}^{L}\sum_{k=1}^{K}(l-\frac{1}{2}k)^4(l^2-kl+k^2)^{-(\nu+4)/2}}{\sum_{l=0}^{L}\sum_{k=1}^{K}(l^2+kl+k^2)^{-\nu/2}+\sum_{l=0}^{L}\sum_{k=1}^{K}(l^2-kl+k^2)^{-\nu/2}}\ , \tag{34}$$

while $\nu=m,n$ and L,K are functions of N.

It turns out that $f_h(n,N)$ is independent of the number N and that it is equal to

$$f_h(n,N)=f_h(n)=\tfrac{3}{8}(n+2)\ . \tag{35}$$

Therefore, the condition of stability [Eq. (33)] reduces to the inequality

$$\tfrac{3}{8}(m+2)>\tfrac{3}{8}(n+2) \tag{36}$$

which is fulfilled for each pair (n,m) if $m>n$.

The hexagonal monatomic structure is stable, as it was previously expected, for all the possible potentials of the form given by Eq. (21). The stability is independent of the potential parameters.

C. Diatomic square lattice

Let us consider a structure in which the unit cell consists of two kinds of atoms denoted as 1 and 2, respectively [see Fig. 1(c)]. The interaction potential now has a form often used in this kind of calculation

$$V(r)=-A_1r_{11}^{-n}-A_2r_{22}^{-n}-2r_{12}^{-n}\sqrt{A_1A_2}+B_1r_{11}^{-m}+B_2r_{22}^{-m}+2r_{12}^{-m}\sqrt{B_1B_2} \tag{37}$$

with $m>n$. The parameters A_1 and A_2 describe the attraction and the parameters B_1 and B_2 describe the repulsion of atoms of the same kind, respectively.

With the above form of the interaction, the potential-energy density is

$$u=-\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}\frac{2(A_1+A_2)}{a^n(l^2+k^2)^{n/2}}-\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\frac{4\sqrt{A_1A_2}}{a^n[(l+\frac{1}{2})^2+(k+\frac{1}{2})^2]^{n/2}}$$
$$+\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}\frac{2(B_1+B_2)}{a^m(l^2+k^2)^{m/2}}+\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\frac{4\sqrt{B_1B_2}}{a^m[(l+\frac{1}{2})^2+(k+\frac{1}{2})^2]^{m/2}}\ . \tag{38}$$

The condition for the energy minimum now yields

$$\frac{n}{m}a^{m-n}=\frac{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(B_1+B_2)(l^2+k^2)^{-m/2}+2\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\sqrt{B_1B_2}[(l+\frac{1}{2})^2+(k+\frac{1}{2})^2]^{-m/2}}{\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(A_1+A_2)(l^2+k^2)^{-n/2}+2\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\sqrt{A_1A_2}[(l+\frac{1}{2})^2+(k+\frac{1}{2})^2]^{-n/2}}\ . \tag{39}$$

The stability of the diatomic square structure requires that [see Eq. (19)]

$$c_{11}-c_{12}=\frac{2a^4}{v_a}\left[-\frac{n}{2}\left[\frac{n}{2}+1\right]a^{-2n}\left[\sum_{l=1}^{\infty}(A_1+A_2)l^{-n}+2\sum_{l=1}^{\infty}\sum_{k=1}^{\infty}(A_1+A_2)(l^4-l^2k^2)(l^2+k^2)^{-(n+4)/2}\right.\right.$$
$$\left.+4\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\sqrt{A_1A_2}[(l+\tfrac{1}{2})^4-(l+\tfrac{1}{2})^2(k+\tfrac{1}{2})^2][(l+\tfrac{1}{2})^2+(k+\tfrac{1}{2})^2]^{-(n+4)/2}\right]$$
$$+\frac{m}{2}\left[\frac{m}{2}+1\right]a^{-m}\left[\sum_{l=1}^{\infty}(B_1+B_2)l^{-m}+2\sum_{l=1}^{\infty}\sum_{k=1}^{\infty}(B_1+B_2)(l^4-l^2k^2)(l^2+k^2)^{-(m+4)/2}\right.$$
$$+4\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\sqrt{B_1B_2}[(l+\tfrac{1}{2})^4-(l+\tfrac{1}{2})^2(k+\tfrac{1}{2})^2]$$
$$\left.\left.\times[(l+\tfrac{1}{2})^2+(k+\tfrac{1}{2})^2]^{-(m+4)/2}\right]\right]>0\,. \tag{40}$$

Let us introduce the following notation:

$$\begin{aligned}
S_1(C,\nu)&=\sum_{l=1}^{\infty}(C_1+C_2)l^{-\nu}\,,\\
S_1\left[C,\frac{\nu+4}{2}\right]&=\sum_{l=1}^{\infty}\sum_{k=1}^{\infty}(C_1+C_2)(l^4-l^2k^2)(l^2+k^2)^{-(\nu+4)/2}\,,\\
S_2\left[C,\frac{\nu+4}{2}\right]&=\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\sqrt{C_1C_2}[(l+\tfrac{1}{2})^4-(l+\tfrac{1}{2})^2(k+\tfrac{1}{2})^2][(l+\tfrac{1}{2})^2+(k+\tfrac{1}{2})^2]^{-(\nu+4)/2}\,,\\
S_1\left[C,\frac{\nu}{2}\right]&=\sum_{l=0}^{\infty}\sum_{k=1}^{\infty}(C_1+C_2)(l^2+k^2)^{-\nu/2}\,,\\
S_2\left[C,\frac{\nu}{2}\right]&=\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\sqrt{C_1C_2}[(l+\tfrac{1}{2})^2+(k+\tfrac{1}{2})^2]^{-\nu/2}\,,
\end{aligned} \tag{41}$$

where $C=A$ or $C=B$, i.e., $C_1=A_1$, $C_2=A_2$, or $C_1=B_1$, $C_2=B_2$, where needed, $\nu=n$ or m.

Then the condition given by Eq. (40) transforms, with the use of Eq. (39), to

$$\frac{(m+2)\left[S_1(B,m)+2S_1\left[B,\frac{m+4}{2}\right]+4S_2\left[B,\frac{m+4}{2}\right]\right]}{S_1\left[B,\frac{m}{2}\right]+2S_2\left[B,\frac{m}{2}\right]}>\frac{(n+2)\left[S_1(A,n)+2S_1\left[A,\frac{n+4}{2}\right]+4S_2\left[A,\frac{n+4}{2}\right]\right]}{S_1\left[A,\frac{n}{2}\right]+2S_2\left[A,\frac{n}{2}\right]}\,. \tag{42}$$

If the atom-atom interactions are limited to the first-nearest neighbors only, both the left-hand and the right-hand sides of inequality (42) are equal to zero. The diatomic square lattice is unstable in this case for all possible values of the potential parameters.

The inequality (42) cannot be generally solved for the number $N\geq 2$ of the coordination spheres. We shall, therefore, introduce a simplification to make it tractable. Let us assume at the beginning that the parameters of the atom1-atom1 interactions only slightly differ from the analogous parameters of the interactions of the atoms of type 2. It allows us to replace the geometric average by the arithmetic one

$$\begin{aligned}
\sqrt{A_1A_2}&\cong\tfrac{1}{2}(A_1+A_2)\,,\\
\sqrt{B_1B_2}&\cong\tfrac{1}{2}(B_1+B_2)\,.
\end{aligned} \tag{43}$$

Now the condition (42) simplifies to

$$\frac{(m+2)\left[S_1(m)+2S_1\left[\frac{m+4}{2}\right]+2S_2\left[\frac{m+4}{2}\right]\right]}{S_1\left[\frac{m}{2}\right]+S_2\left[\frac{m}{2}\right]}$$
$$>\frac{(n+2)\left[S_1(n)+2S_1\left[\frac{n+4}{2}\right]+2S_2\left[\frac{n+4}{2}\right]\right]}{S_1\left[\frac{n}{2}\right]+S_2\left[\frac{n}{2}\right]}\,. \tag{44}$$

The quantities $S_i(\nu)$, $i=1,2$ in inequality (44) are defined by Eq. (41) with one difference: all parameters C, C_1, C_2

should simply be omitted. As in the case of the monatomic square lattice, each side of the inequality (44) is given by the same functions of two parameters: n (or m) and the number N of the coordination sphere limiting the interactions of atoms. Several functions $f_D(n,N)$ are shown in Fig. 4. This figure is very similar to that for the simple square lattice (Fig. 2). In the approximation defined in Eq. (43), the diatomic square lattice is, therefore, stable for the same values of n, m, and N as the monatomic square structure.

If the approximation given by Eq. (43) does not hold, the diatomic square lattice can nevertheless be stable when the interaction parameters A_1, A_2, B_1, and B_2 fulfill a certain relation. With the use of condition (42), it is possible to obtain this relation for defined values of n, m, and N—the largest distance of the atom-atom interactions.

With only first- and second-nearest-neighbor interactions, the inequality (42) reduces to

$$\beta > \frac{2(2^m)^{1/2}(n+2)\alpha}{(m-n)\alpha + 2(2^n)^{1/2}(m+2)} , \tag{45}$$

where

$$\beta = \sqrt{B_1/B_2} + \sqrt{B_2/B_1}, \quad \alpha = \sqrt{A_1/A_2} + \sqrt{A_2/A_1} . \tag{46}$$

Assuming that $A_1 > A_2$ and $B_1 > B_2$, one can find the minimal values of B_1/B_2 needed to get the stable structure for given values of A_1/A_2, n, and m. These values are quoted in Table I with the accuracy 0.1.

It can be seen from Table I that B_1/B_2 is much higher than A_1/A_2 for a large number of quoted examples. Using the Lennard-Jones-type formula for the potential

$$V_{\mathrm{LJ}}(r) = -\left[\frac{\sigma_1}{r_{11}}\right]^n - \left[\frac{\sigma_2}{r_{22}}\right]^n - 2\left[\frac{(\sigma_1\sigma_2)^{1/2}}{r_{12}}\right]^n + \left[\frac{\sigma_1}{r_{11}}\right]^m + \left[\frac{\sigma_2}{r_{22}}\right]^m + 2\left[\frac{(\sigma_1\sigma_2)^{1/2}}{r_{12}}\right]^m , \tag{47}$$

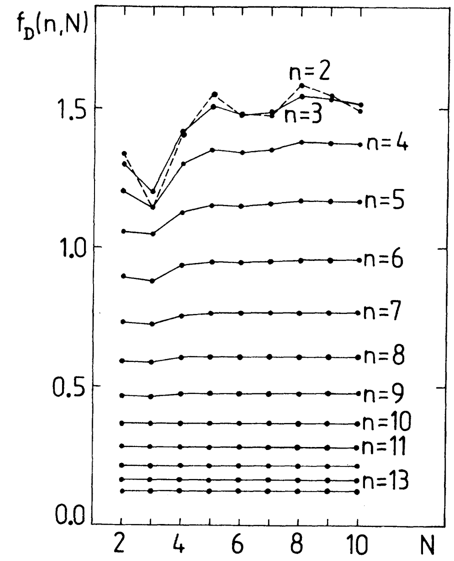

FIG. 4. Quantity $f_D(n,N)$ [see Eq. (44)] for a diatomic square lattice as a function of the maximal range of interactions N and calculated for several values of exponent n. Lines are given to guide the eyes.

i.e., $\sigma_1^n = A_1$, $\sigma_2^n + A_2$, $\sigma_1^m = B_1$, and $\sigma_2^m = B_2$, one gets the following relation:

$$\frac{B_1}{B_2} = \left[\frac{A_1}{A_2}\right]^{m/n} . \tag{48}$$

For $n=2$ and 3, the stability of the lattice is attained if $m < 3n$ and A_1 is a few times greater than A_2 (see Table I). For $n=6$ and $m=12$, the diatomic square lattice can now be stable only if $A_1/A_2 > 20$.

The inclusion of the third-nearest-neighbor interactions yields the following condition of stability:

$$\beta > \frac{2(n+2)\alpha 2^{m/2}}{(m-n)\alpha + (m+2)\alpha 2^{-n/2} - (n+2)\alpha 2^{-m/2} + 2(m+2)2^{n/2}} . \tag{49}$$

β and α are given by Eq. (46). The minimal values of B_1/B_2 (with the accuracy 0.1), which assure the mechanical stability of the lattice for the potential function [Eq. (37)] with $n=6$ and $m=12$, are now quoted in Table II. They are denoted as $(B_1/B_2)_{\mathrm{III}}$. The respective values of $(B_1/B_2)_{\mathrm{II}}$ obtained for the same form of the potential with the interactions limited to the second-nearest neighbors are also given for comparison in Table II. The similarity of the values $(B_1/B_2)_{\mathrm{III}}$ and $(B_1/B_2)_{\mathrm{II}}$ shows that the inclusion of the subsequent interacting neighbors does not change the qualitative results obtained for $N=2$.

The differences between $(B_1/B_2)_{\mathrm{III}}$ and $(B_1/B_2)_{\mathrm{II}}$ turn out slightly greater for lower values of the exponents n and m than in the above case. For $n=2$ and $m=3$, the structure can be stable even for the monatomic lattice ($A_1 = A_2$, $B_1 = B_2$; see Fig. 4). Some other examples of $(B_1/B_2)_{\mathrm{III}}$ for $n<6$ are given in Table III (the accuracy is 0.1). The results can be summarized as follows. If the atoms of type 1 and 2 interact through potentials characterized by similar parameters, the diatomic square lattice can only be stable if $n=2$ and $m=3$ and $N=3$, 4, 7, and 10.

TABLE I. The minimal values of B_1/B_2 which can stabilize the diatomic square lattice for the potential given by Eq. (37). The interactions to the second-nearest neighbors are taken into account.

n	m	$\frac{A_1}{A_2}$	$\frac{B_1}{B_2}$	n	m	$\frac{A_1}{A_2}$	$\frac{B_1}{B_2}$	n	m	$\frac{A_1}{A_2}$	$\frac{B_1}{B_2}$
2	3	1	1.7	3	4	1	2.6	4	6	1	5.8
2	3	2	2.3	3	4	2	3.3	4	6	2	6.8
2	3	4	4.1	3	4	6.8	8.5	4	6	6.8	14.9
2	3	6.8	6.6	3	4	34	34.1	4	6	14	26.5
2	3	14	12.2	3	4	100	80.9	4	7	1	10.1
2	3	34	25.3	3	5	1	4.5	4	7	2	11.5
2	3	62	39.8	3	5	2	5.3	4	7	6.8	23.3
2	3	100	54.9	3	5	4	8	4	8	1	17
2	4	1	2.9	3	5	6.8	11.8	4	8	2	19.2
2	4	2	3.5	3	5	100	88.1	4	8	6.8	37.2
2	4	4	5.5	3	6	1	7.7	5	7	1	6.8
2	4	6.8	8.2	3	6	2	8.7	5	7	2	8
2	4	14	14	3	6	4	12.3	5	7	14	31.3
2	4	34	26.4	3	6	6.8	17.6	5	8	1	12.1
2	4	100	50.9	3	6	100	111	5	8	4	19.5
2	5	1	4.9	3	7	1	12.7	5	9	1	20.9
2	5	2	5.7	3	7	4	19.6	5	10	1	35.8
2	5	4	8.1	3	7	6.8	27.1	5	10	2	40.1
2	5	34	32.8	3	7	14	43.8	5	10	14	130.4
2	5	100	58.9	3	8	1	21	5	10	100	580
2	6	1	8.2	3	8	4	31.6	6	8	1	7.7
2	6	2	9.2	3	8	6.8	43	6	8	2	8.9
2	6	4	12.4	3	8	14	67.9	6	8	14	35.2
2	6	14	26.4	3	9	1	35.2	6	8	34	77.8
2	6	100	77	3	9	4	51.7	6	12	1	73.3
2	7	1	13.2	3	9	6.8	70	6	12	2	82.2
2	7	2	14.9	3	9	14	108.2	6	12	4	112.8
2	7	4	19.7	4	5	1	3.3	6	12	6.8	159.2
2	7	14	39.8	4	5	2	3.9	6	12	14	270.8
2	7	100	108.7	4	5	14	18.5	6	12	34	556.5
2	8	1	22.2	4	5	62	70	6	12	62	905.1
2	8	4	31.9	4	5	100	103.8	6	12	100	1298

TABLE II. The minimal values of $(B_1/B_2)_{\text{III}}$ and $(B_1/B_2)_{\text{II}}$ for the interactions to the third- and the second-nearest neighbors, respectively, for the potential given by Eq. (37) with $n=6$ and $m=12$.

$\frac{A_1}{A_2}$	$\left[\frac{B_1}{B_2}\right]_{\text{II}}$	$\left[\frac{B_1}{B_2}\right]_{\text{III}}$	$\frac{A_1}{A_2}$	$\left[\frac{B_1}{B_2}\right]_{\text{II}}$	$\left[\frac{B_1}{B_2}\right]_{\text{III}}$
1	73.3	71.3	14	270.8	257.1
2	82.2	79.7	34	556.5	516.8
4	112.8	109	62	905.1	824.3
6.8	159.2	152.9	100	1298.1	1161.2

TABLE III. The minimal values of $(B_1/B_2)_{\rm III}$ and $(B_1/B_2)_{\rm II}$ for the interactions to the third- and the second-nearest neighbors, respectively, for the potential given by Eq. (37) with different values of n and m.

n	m	$\frac{A_1}{A_2}$	$\left[\frac{B_1}{B_2}\right]_{\rm II}$	$\left[\frac{B_1}{B_2}\right]_{\rm III}$
2	4	1	2.9	1.1
2	5	1	4.9	2.9
2	6	1	8.2	5.3
2	7	1	13.2	9
2	8	1	22.2	15.3
3	4	1	2.6	2
3	4	2	3.3	2.7
3	5	1	4.5	3.6
3	6	1	7.7	6.2
3	7	1	12.7	10.3
3	8	1	21	16
4	5	1	3.2	2.9
4	6	1	5.8	5.3
4	7	1	10.1	9
4	8	1	17	15.3
4	9	1	28.7	25.8
5	6	1	3.6	3.5
5	7	1	6.8	6.1
5	8	1	12.1	12.1
5	9	1	20.9	19.8

Another possibility of the lattice to be stable is that the relation (42) is fulfilled but the assumption (43) is not. For example, when $N=2$, the inequality (42) reduces to formula (45), which is usually satisfied for $B_1/B_2 \gg A_1/A_2$.

IV. DISCUSSION

The calculation of the elastic constants presented in Sec. III shows that the square monatomic lattice is unstable for the majority of the atom-atom potentials of the form given by Eq. (21). The instability which is related to a negative value of $c_{66}=c_{12}$ shows a tendency of the lattice to transform its unit cell into a rhombus. When the acute angle of the rhombus acquires the value of 60°, one obtains a hexagonal structure—the structure of the lowest energy for planar lattices.

The instability of the square lattice remains valid for all the coefficients A,B and all the exponents n,m except for $n=2$ and $m=3$. In this latter case the monatomic square lattice is stable if one restricts the interactions to specific numbers of coordination spheres. The form of the potential with $n=2$ and $m=3$ is, however, rather special and is conceivable only if one takes into account some interactions highly mediated by the underlying bulk lattice. In fact, the (001) surfaces of atomic crystals very seldom show a planar square structure as it should be if they were unreconstructed. The experimental observations[15] indicate that the latter surfaces are rough or stepped.

The diatomic square lattice can be stable for the potential of the form given by Eq. (37) if the ratio of the repulsive parameters B_1/B_2 is sufficiently high [the inequality (42) is then fulfilled]. This condition means that there is a great difference between the atom1-atom1 and the atom2-atom2 interactions. If the inequality (42) is not fulfilled, the diatomic square lattice is unstable. The instability is related to a negative value of $c_{11}-c_{12}$. It means that the lattice has a tendency to transform its unit cell into a rectangle and finally into a 60° rhombus (see also Ref. 12 for a discussion of this instability).

Mechanical stability does not exhaust the problem of the general stability of the lattice. The structure may well be unstable at different points of the Brillouin zone even though the conditions of the mechanical stability were fulfilled. An insight into the atomic displacements at some highly symmetrical points of the Brillouin zone boundary shows that, up to the second-nearest interacting neighbors, the structure remains stable whenever it is mechanically stable. Indeed, in the monatomic square lattice, the changes in the atomic distances corresponding to the uniform shear are the same as those corresponding to the transverse acoustic mode at $\mathbf{k}=(0,\pi/a)$. Thus, the zone-center and the zone-boundary instabilities occur simultaneously. The same happens at the $\mathbf{k}=(\pi/a,\pi/a)$ point where half of the first-nearest-neighbor distances are shortened, the other half are elongated and half of the second-nearest-neighbor distances are elongated in the transverse vibration. Since, in the mechanically stable lattice, the first-nearest-neighbor distance is shorter than that of the minimum of the interatomic potential and the second-nearest neighbors lie between the minimum and the inflection point, the distortion corresponding to the TA at the $(\pi/a,\pi/a)$ point always increases the potential energy. The same can be stated on the diatomic square lattice; it is then enough to interchange the (1,1) and (1,0) directions. In case of the longer range of interactions, a more specific analysis is needed to reveal the global stability of the lattices.

It follows from experiments on (001) crystal surfaces of diatomic fcc crystals[16] that the square symmetry of the surface is usually stabilized by steps, i.e., the square structures are seldom stable in real systems.

The two-dimensional lattices cannot always give the description of the surface layers in crystals. The interaction between the topmost layer and the deeper layers should then sometimes be taken into account. The discussion on the stability of the square planar structures can, however, elucidate the problem of the absence of the square symmetry planar surfaces observed in real crystals.

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