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Substrate-induced pairing of Si ad-dimers on the Si(100) surface

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Abstract

The interaction between Si ad-dimers on the Si(100) surface has been studied by total-energy calculations with a three-particle Stillinger–Weber potential. We have found a strong attractive interaction between neighboring Si ad-dimers located in neighboring on-top and deep-channel positions in adjacent substrate dimer rows. This should result in a four-atomic block consisting of two dimers as an important elementary object of the Si(100) kinetics. © 1997 Elsevier Science B.V.

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1. Introduction

The Si(100) surface is one of the most important surfaces from a technological as well as a scientific point of view. During the last decade it has been studied intensively with both experimental and theoretical methods. It is well known that the Si(100) surface reconstructs to form rows of dimerized atoms, yielding a $p(2\times1)$ unit cell. This surface is always stepped because it is virtually impossible to cut the crystal exactly along the (001) plane. Moreover, even the ideal surface (the surface without steps) is unstable with respect to step creation [1,2]. The steps play a very important role in crystal growth, acting as sinks for incoming Si atoms in epitaxial growth. However, even the most fundamental questions about elementary processes of the initial growth of Si on Si(100), as well as that of step kinetics are not fully understood yet.

The $p(2\times1)$ structure of the Si(100) surface is characterized by two types of "channels", the "on-top channels" which are on top of the substrate dimer rows, and the "deep channels" in between the dimer rows. At present, a realistic scenario of initial stage of the Si(100) growth is the following [3–6]: Two Si ad-atoms which diffuse along the on-top channel can easily find one another and form a dimer (ad-dimer). At temperatures $T<100$ °C this dimer is moving (and rotating) in the on-top channel [3,7]. After annealing at temperatures above 125 °C, most of the Si-blobs are found in the deep channels as follows from filled state STM images (although it is at present not fully clear whether or not this is indeed the lowest energy channel). Thus, at room temperatures and above the Si ad-dimers play a key role. The main

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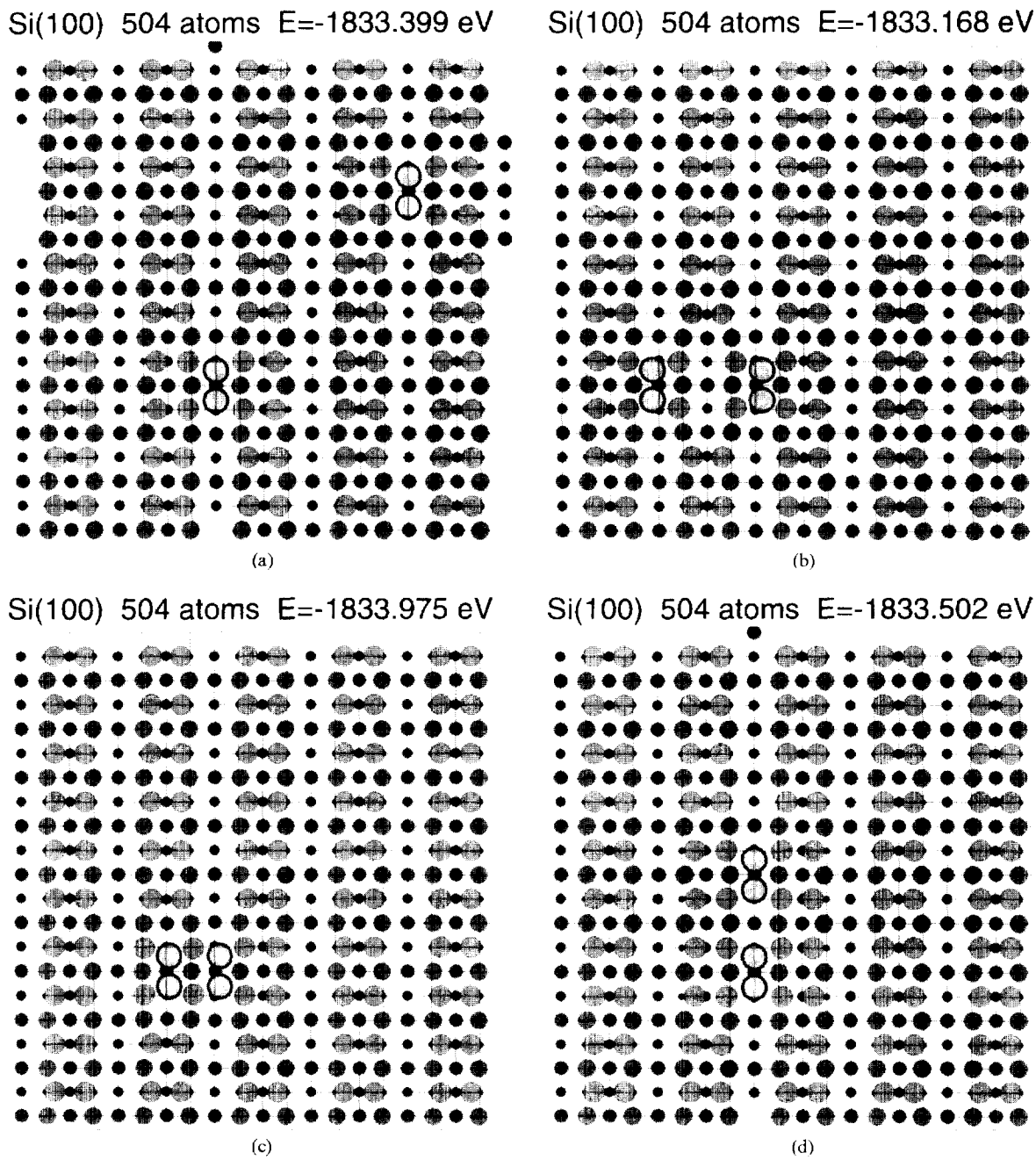

Fig. 1. Four different adsorption configurations for two Si ad-dimers on the Si(100) surface. The sizes of atoms are proportional to their z coordinate, and the gray-scale corresponds to the layer's number (light gray for top ad-dimers to black for the deepest fifth layer of the substrate). The ad-dimers on the slab are indicated with thick circles. (a) Two dimers are situated "far" from one another; (b) the ad-dimers are close to one another lying in the nearest deep channels; (c) the ad-dimers occupy the nearest neighboring positions, one in the deep channel, and the second in the nearest top channel, so that the two dimers occupy a compact (2×2) region (this block of four Si ad-atoms has the lowest energy and should be considered as the "elementary object"); (d) the dimers are situated in the same deep channel.

goal of the present study is to investigate the interaction between the ad-dimers.

In our calculations we use the empirical Stillinger–Weber (SW) potential [8], because it was carefully tested with bulk Si properties, leads to correct the value of the melting point of Si crystal, and it describes properly not only the Si diamond structure, but the structure of the Si liquid phase as well (the calculated structure factors for the Si liquid phase are in reasonable accordance with experimental data). For the Si(100) surface, the SW potential gives the $p(2\times1)$ reconstruction. Besides, the Stillinger–Weber calculations [3] reveal that the energetically most favorable configuration corresponds to the ad-dimer sitting in the deep channel, i.e. between the substrate dimer rows. Although at present it is not fully clear whether or not this is indeed the lowest energy channel for a single ad-dimer, it holds true for a step with kinks which always is ended with dimers sitting in deep channels.

An alternative approach [9,10] based on "first-principle" quantum mechanics, gives the Si diamond structure and the $p(2\times1)$ reconstruction as well and, moreover, it correctly predicts the buckling of dimers on the Si(001) surface. Unfortunately, this method can be used for systems containing a relatively small number of atoms only. Furthermore, the "first-principle" method predicts that a position in the on-top channel is the most favorable one for an ad-dimer. This, however, seems to disagree with the available experimental data [3,6] discussed above.

In the present study the substrate was modeled by a five-layer slab, each layer has the 10×10 structure, so in total the substrate contains 500 atoms. We apply the periodic boundary conditions along the surface, and also couple the atoms of the lowest layer to their "ideal" positions by springs with the elastic constant equal to that of the pairwise part of the SW potential. All atoms are allowed to move and the system relaxes to a nearest minimum of the total potential energy (for detail see Refs. [18,21,22]). The system without ad-atoms exhibits the $p(2\times1)$ reconstruction with a distance between the atoms forming the dimer of 2.40 Å. The additional Si atoms were then positioned on this slab.

Table 1

Configuration	ΔE(eV)		h(Å)		a_{dimer}(Å)
	Our	Zhang et al.[3]	Our	Zhang et al.[3]	Our
In the deep channel					
F–F	–	–	0.97	0.96	2.40
D D*	0.78	0.79	1.49	1.36	2.45
In the top channel					
B–B	0.82	0.86	1.35	1.35	2.41
D D	0.91	0.92	1.86	1.85	2.40

To test our program, we first repeated calculations for the configurations previously studied in Ref. [3], i.e. the configurations with 502 atoms, where a single ad-dimer is placed on the five-layer slab at different positions. We confirmed that the most stable dimer configuration corresponds to the dimer situated in a deep channel and oriented along it. The results of the calculation are summarized and compared with those of Ref. [3] in Table 1. A slight difference between our and Zhang et al.'s [3] results may be accounted to different boundary conditions (periodic boundary conditions in the present study versus free-boundary conditions in Ref. [3]).

2. Interaction between dimers

To study the interaction between the ad-dimers, we calculated the energies of several configurations (all containing 504 atoms) having two dimers adsorbed on the five-layer Si slab. The first configuration, where the dimers are situated "far" one from another, see Fig. 1a, is used as the reference configuration. The next three configurations shown in Fig. 1b–d, describe two dimers which are situated close to each other. Namely, Fig. 1b corresponds to the situation when both dimers are in the neighboring deep channels (i.e. in the most favorable sites for a single dimer according to the SW calculations) and are close to one another. Comparing the energies of configurations of Figs. 1a and b, one can see that these two neighboring dimers strongly repel each other, the energy of repulsion is 0.23 eV.

On the other hand, when the dimers occupy the nearest neighboring channels, one lying in the deep channel and another in the top one, see Fig. 1c, so that the position of the second dimer is quite unfavorable from the single-dimer point of view, these two dimers exhibit a very strong attraction, the interaction energy is −0.58 eV. This can be understood [11] if we recall that the substrate atoms below the ad-dimers, undergo a local dereconstruction, their positions are close to those in the ideal diamond structure as is immediately clear from Fig. 1. The dereconstruction, obviously, increases the system energy. But when the two dimers cover a compact (2×2) region on the surface, an essential part of the dimerization energy is recaptured owing to reconstruction of the newly created top layer.

Finally, when two dimers occupy the same deep channel, see Fig. 1d, they weakly attract one another with the interaction energy of −0.1 eV. Besides, we calculated the energy of interaction between two dimers when both of them are lying in top channels. In this case the dimers are repelling with the energy of 0.01 eV when they are in the same channel, and with the energy of 0.18 eV when they occupy the adjacent top channels. Note that the result that the configuration of Fig. 1c corresponds to the minimum of the system potential energy, agrees with the "first-principle" calculations of Ref. [10].

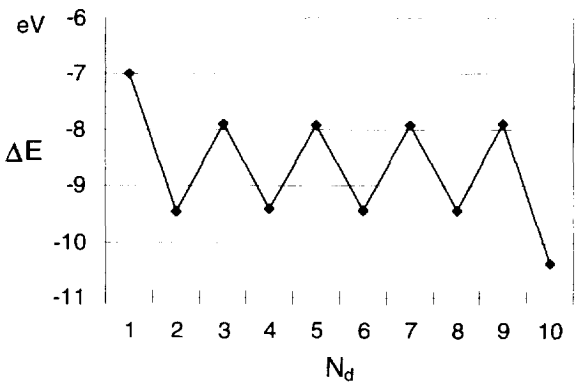

Fig. 2. Energy difference Eq. (1) of the dimers' row oriented perpendicularly to underlying substrate rows, versus the length of the row. The row begins with an ad-dimer in the on-top channel. Observe the large decrease in energy when the last dimer is added to fill the row completely.

Now let us compare the simulation results with the available experimental data. The molecular beam epitaxy experiments [12,13] for temperatures around 500 K show that at an initial stage one-dimensional dense-dimer rows oriented perpendicular to the substrate dimer rows, grow into long strings. This is in agreement with our prediction based on the interaction between the dimers.

To check this conclusion in more detail, we made a series of simulations for a dimer row of increasing length, the row being oriented perpendicular to the underlying substrate rows. We calculated the energies $E(N_d)$ of configurations of $500+2N_d$ atoms, N_d being the number of dimers in the row. In Fig. 2 we plot the energy differences

$$\Delta E(N_d) = E(N_d) - E(N_d - 1). \quad (1)$$

$N_d = 1$ corresponds to one dimer in the on-top channel and $N_d = 10$ and is the maximum number of dimers in our system, when the row closures into ring. Adding one dimer at a time, we see that the energy $\Delta E(N_d)$ oscillates with the length. It reaches local minima for the configurations with even number of dimers, the end dimer at the growth side occupying the deep channel. Thus, the simulation predicts that a dimer in the deep channel should work as a "nucleus" which then adds itself more and more blocks of two ad-dimers.

This conclusion is confirmed by the fact that the energy gain of adding a dimer block to the row, e.g. $\Delta E(3)+\Delta E(4)$ is bigger than the energy gain $\Delta E(1)+\Delta E(2)$ of adding one block to the slab.

The interaction energies between the ad-dimers can also be extracted from a statistical analysis of the step edge roughness [6,16]. The approach is as follows: the concentration of kinks of various lengths is compared with that predicted by a simple Boltzmann distribution. This analysis of the roughness of the step edges gives an attractive interaction energy of 0.38 eV between two neighboring dimers within a row, whereas an attractive interaction energy of 0.12 eV between dimers in adjacent dimer rows is found [14]. These numbers are in reasonable agreement with the theoretical calculations (0.58 eV vs 0.38 eV and 0.1 eV vs 0.12 eV, respectively).

To summarize, the main result of this section is that a block of two dimers forms an energetically

favorable configuration: such a block has lower energy than a configuration with the two dimers apart. Also, for a block it is more favorable to lengthen a row, rather than staying alone.

3. Step with two kinks

We have calculated the energies of four configurations which model the Si(100) surface containing a single surface step. Recall that the p(2×1) structure exhibits two types of steps, the so-called A-type steps which are running parallel to the dimer rows of the upper terrace, and the B-type steps oriented in the perpendicular direction. We choose the A-type step because these steps are more stable, the STM pictures show that A-type steps are almost straight, while the B-type steps are always ragged. First we prepared the corresponding initial configuration to model the A-type step with two kinks. We choose an odd (five) number of dimers in the step, in accordance with the results of dimer-row simulations described above, and also taking into account that the experimental data show that the kinks on the A-type step are always ended by deep-channel dimers. The relaxed configuration shown in Fig. 3a is used as the reference configuration. Next we calculated the energies of three other configurations presented in Figs. 3b–d.

In the configuration of Fig. 3b we released from the step the last (end) dimer, and put it into the deep channel "far" away from the step. Comparing the energies of Figs. 3a and b we see that this process requires an energy $\Delta E = 1.09$ eV.

Next, we release the second dimer from the step end, i.e. the dimer which occupies the unfavorable top channel, and again put it into the deep channel "far" away from the step. As seen from Fig. 3c, this process costs $\Delta E = 1.96$ eV and, therefore, seems to be quite expensive.

Last, we removed from the end of the step the "elementary" four-atomic block, i.e. two end dimers simultaneously, and put them into adjusted deep channels, again "far" away from the step. The resulting relaxed configuration is presented in Fig. 3d. Comparing with the reference configuration of Fig. 3a one sees that this process needs an energy of $\Delta E = 1.50$ eV. We see that this is more expensive than removing the end dimer of the step (b), but cheaper than removing the "near end" dimer (c).

Now let us recall that the two dimers situated in the adjusted deep channels (see Fig. 1b), strongly repel each other, while those for the "elementary" block (Fig. 1c), on the contrary, are attracting, so that the transition from the configuration of Fig. 1b to the configuration of Fig. 1c leads to an energy gain of $\Delta E_1 = 0.23 + 0.58 = 0.81$ eV. Thus, it is easy to conclude that if we will remove from the step end the "elementary" block of two dimers and left it to remain as a whole block (not allowing to dissociate into separate dimers), this process will cost only $\Delta E = 1.50 - 0.81 = 0.69$ eV. Consequently the process of removing of the whole "elementary" four-atomic block should be the most favorable one.

This result is in agreement with the high temperature STM data of Si(001) [11,15,17]. In these experimental high temperature studies it was shown that the step motion of Si(001) always occurs in units of two dimers, i.e. four surface atoms. For a clear illustration see the STM photographs in Ref. [15]: kinks in step edges always end in between two dimer rows in the underlying surface. Besides, Pearson et al. [11] measured the kink diffusion coefficient in the temperature interval of 520–700 K. According to their results, it is equal to $D = \nu \exp[-(0.97 \pm 0.12\ \text{eV})/kT]$, the prefactor ν being in the range 4×10^4 to $3 \times 10^6\ \text{s}^{-1}$, i.e. it is characterised by a very small prefactor as could be expected for the concerted motion of a large block.

4. Discussion

In summary, we showed that the energetically most favorable equilibrium configurations are obtained when ad-dimers join into pairs, thus forming blocks of four ad-atoms.

A natural question then is if such a block can be considered as the elementary unit during the kinetic processes. In connection with this we have to emphasize that the Si dimers should not be considered as "molecules" slowly interacting with

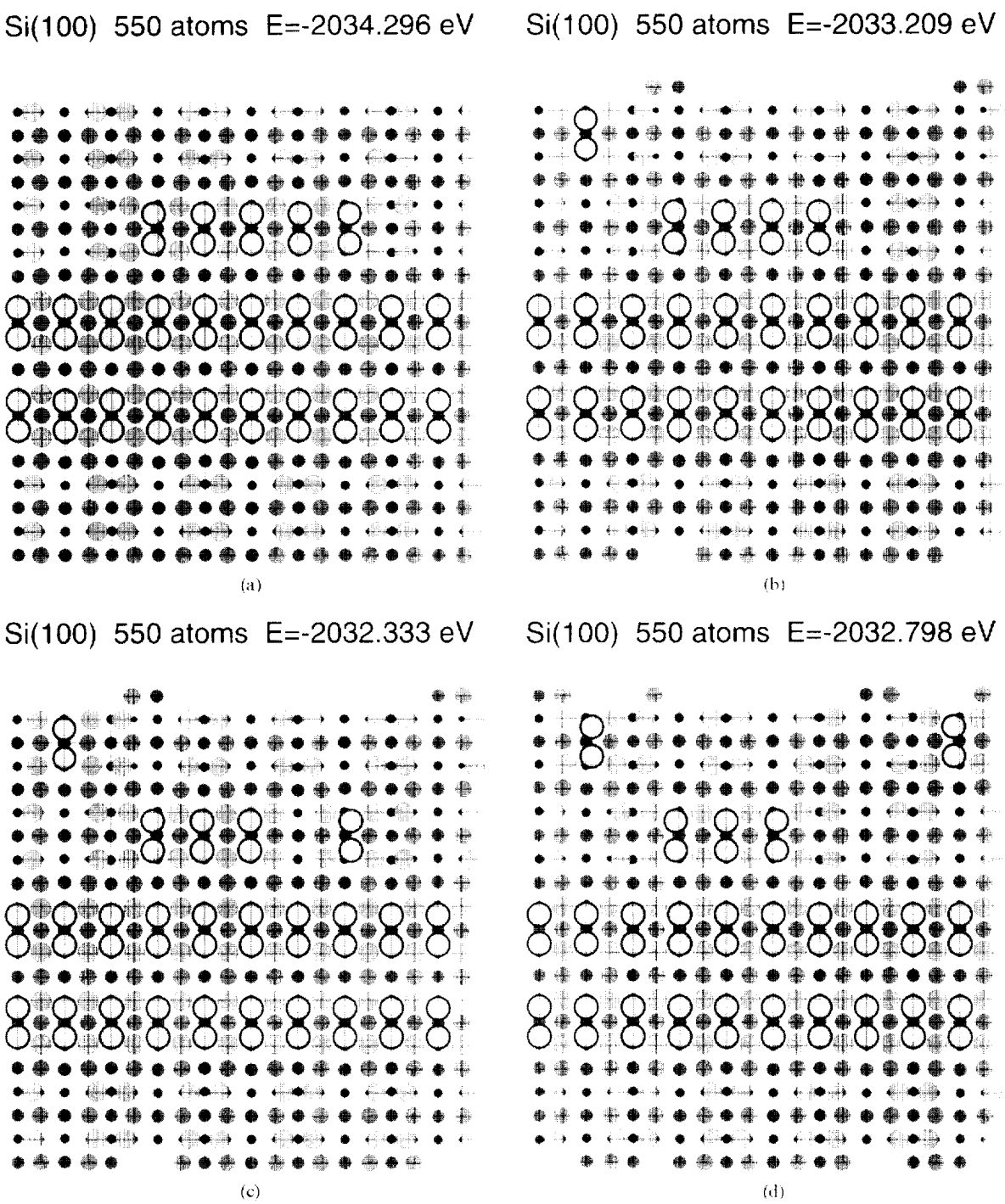

Fig. 3. (a) Half-covered Si(100) surface with the A-type step and two kinks; (b) the end dimer from the step is released and put into the deep channel "far" away from the step; (c) the dimer second from the step end, is taken out and put into the deep channel "far" away from the step; (d) the "elementary" block of four Si atoms is taken away from the step, the block is then split into two dimers which are put into the neighboring deep channels "far" away from the step.

a pairwise potential. The three-atomic contribution to the interaction potential plays, via the substrate, the dominant role in the formation of the blocks and their dynamics.

The question above cannot be answered positively on the basis of the present work. We were able to calculate the energies of stable configurations only. But to estimate a rate of kinetic processes, we need to know also the energies of saddle (unstable) configurations. Such type of calculation may be done in a relatively simple way for the case of motion of a single atom or dimer (e.g. see Ref. [19]), but becomes quite complicated for the case of a concerted motion of four atoms in three-dimensional space. Besides, the zero-temperature saddle energies may differ essentially from real values of activation barriers at nonzero temperatures because of several factors (for detail see Ref. [20]).

More reliable results may be extracted from Langevin-type simulations. But the following two factors make the feasibility of this type of simulation questionable for the system under consideration. First, trio interaction takes more computer time than a conventional pairwise interatomic potential used usually in molecular dynamics simulations. The second and more important point is that the concerted motion of the four-atomic block is expected to be characterised both by a lower activation barrier, as well as by an Arrhenius prefactor much lower than for single-atomic diffusion [11]. Pearson [11] obtained experimentally quite small preexponential factors like that of $10^5\ s^{-1}$ for the dynamics of kinks, which was seen to be governed by dimer blocks. Therefore, the concerted motion becomes dominant only at low enough temperatures. But the lower the temperature, the longer the simulation needed time to observe at least one diffusion event for the four-atomic block. The simulation times available for us in the present work, were about 10^{-10} s, and that certainly is too short for study of the concerted diffusion. However, we hope to overcome this problem in future work.

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