PHYSICAL REVIEW B VOLUME 51, NUMBER 23 15 JUNE 1995-I

Frenkel-Kontorova model with a nonconvex transverse degree of freedom: A model for reconstructive surface growth

Oleg M. Braun
Institute of Physics, Ukrainian Academy of Sciences, 46 Science Avenue, UA-252022 Kiev, Ukraine

Michel Peyrard
Laboratoire de Physique de l'Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon Cédex 07, France

(Received 18 November 1994)

We study the ground state (GS) of a generalized Frenkel-Kontorova model with a nonconvex transverse degree of freedom. The model describes a lattice of atoms with a given concentration interacting by exponential repulsive or Morse-type forces. The lattice is subjected to a two-dimensional substrate potential which is periodic in one direction and nonconvex (Morse) in the transverse direction. The model exhibits transitions from the trivial (linear) GS to a GS with escaped atoms when the amplitude of repulsion or the concentration of atoms increases. The results are used to describe reconstructive crystal growth which occurs when the growth of the second atomic layer leads to a reconstruction of the underlying first layer, and the "complicated exchange-mediated diffusion mechanism" recently observed in molecular-dynamics simulations [J.E. Black and Zeng-Ju Tian, Phys. Rev. Lett. **71**, 2445 (1993)].

I. INTRODUCTION

In the past decade, the heterogeneous crystal growth of artificial layered materials has been a subject of intense studies because, besides its fundamental interest, it has important applications for microelectronics. Depending on the parameters of the pair substrate-growing crystal, the growth can occur through three mechanisms: first, by the *Frank–van der Merwe* (layer-by-layer) mechanism, second, by the *Vollmer-Weber* mechanism (when separate islands of three-dimensional crystals start to grow from the very beginning), and third, by the *Stranski-Krastanov* mechanism (when the first layer grows by the first mechanism, while the second and subsequent layers grow by the second mechanism).[1] However, precise experiments show that in some systems the growth is a more complicated process. For example, for a lithium film growing on the (112) surface of tungsten or molybdenum the growth of the second layer leads to a reconstruction of the underlying first layer.[2,3]

The growth process is generally investigated in the framework of lattice-gas type models, such as the Ising model for studying the growth of the first layer, and the solid-on-solid (SOS) model for investigation of thin film growth.[4] In particular, a generalized SOS model[5] allows us to simulate all three growth scenario mentioned above. However, the lattice models are oversimplified, because they assume that incoming atoms have to be placed only at fixed points (lattice sites) defined by the substrate. As a result, these models cannot describe a possible incommensurate structure of the first layer and, moreover, they cannot explain more complicated growth scenarios involving crystal reconstruction.

In more realistic models the substrate is considered as the source of a potential which is periodic along the surface, and the incoming atoms are allowed to shift from the minima of this potential. The best known model of this type is the Frenkel-Kontorova (FK) model,[6] where a chain of interacting atoms is subjected to a one-dimensional sinusoidal potential. The FK model was successfully used to describe misfit dislocations and commensurate-incommensurate transitions in the first adsorbed layer [see Ref. 7 and references therein].

The standard FK model assumes that the mean interatomic distance along the chain varies only in a small range, so that the interatomic potential may be expanded in a Taylor series, keeping the square terms only. This harmonic approximation simplifies greatly the analytical studies, but it is sometimes rather crude. To model the growth of a film, a natural variable of the system is the atomic concentration or the dimensionless "coverage" $\theta = N/M$ (where N is the number of atoms and M is the number of minima of the substrate potential). In actual experiments, θ can vary in a very wide interval from $\theta = 0$ to $\theta \sim 1$ during the growth of the first layer, and becomes $\theta > 1$ during the growth of the second and next layers. In this case, the harmonic approximation for the interaction potential $V_{\rm int}(r)$ becomes unrealistic, and a more realistic (i.e., anharmonic) function for the interatomic potential[8] has to be used.

Another serious restriction of the classical FK model is that it assigns a single degree of freedom for an atom, because the atoms are allowed to move only along the chain. This assumption is realistic when we are considering quasi-one-dimensional systems, such as a submonolayer film adsorbed on a furrowed crystal surface at low coverage $\theta \lesssim 1$. But when θ increases so that the atoms begin to use the repulsive branch of their interaction potential, at some critical amplitude of the repulsion, the atoms start to shift in the direction perpendicular to the chain. To describe this situation, we must allow the atoms to move in two or three directions (i.e., along the chain as well as in the transverse directions). Such a generalization of the FK model to describe atoms mobile in a furrow was proposed first in Ref. 9 and then studied in Refs. 10–12. The substrate potential was modeled by a two-dimensional function, sinusoidal along the chain and parabolic in the transverse direction. It was shown that, with increasing interatomic repulsion, the trivial (linear) ground state (TGS) of the system is transformed to a "zigzag" ground state (ZGS), where the nearest-neighboring atoms are displaced in opposite transverse directions. Then the ZGS evolves into more complicated structures[11] if the repulsion continues to rise.

The aim of the present work is to modify the zigzag-FK model in order to describe crystal growth near the $\theta \sim 1$ coverage and above, to study in particular the process leading to the formation of the second layer. This requires two essential modifications of the model. First, the potential in the transverse direction can no longer be treated as parabolic, because the transverse degree of freedom describes now the atomic displacements perpendicular to the surface of the substrate. When an atom moves away from the surface the transverse potential has to tend to a constant, the "vacuum level" for an atom taken away from the surface. As the potential must also exhibit a minimum at the surface level to describe the sticking of the overlayer on the substrate, the transverse potential must be nonconvex, and this will lead to a more complicated model behavior than for the parabolic potential. For the sake of concreteness, we will use the Morse potential for the transverse substrate potential. Second, the purely repulsive interatomic potential used in the previous studies must also be modified to include an attractive branch at large distances, so that the interatomic potential has to be modeled by a nonconvex function too, for example, by a Morse-type potential.

To simplify the investigation, we will generalize the model in two steps: we study first the model with a repulsive interatomic interaction (exponential for the sake of concreteness), but with a Morse transverse potential due to the substrate, and in the second step, we introduce also the nonconvex potential for the interatomic interaction.

The paper is organized as follows. The model, the choice of its parameters, and the numerical method are described in Sec. II. The case of an exponential interatomic repulsion is studied in Sec. III, while a more realistic model with a Morse-type interaction is investigated in Sec. IV, where the process of the growth of an overlayer is considered more precisely. Finally, Sec. V concludes the paper by some discussion of the results. Although the model is presented with a special emphasis on crystal growth, it should be noticed that the generalization of the Frenkel-Kontorova model that we discuss here is also of general interest, because the standard FK model has been the basis for many studies in nonlinear sciences.

II. THE MODEL

The displacement of an atom is characterized by two variables: x describes its motion parallel to the surface and y describes its deviation orthogonal to the substrate. For the potential perpendicular to the surface, let us take the Morse function,

$$V_y(y) = \varepsilon_d \left(e^{-\gamma y} - 1\right)^2, \tag{1}$$

which goes to the finite limit ε_d (known as the adsorption energy) when $y \to \infty$. The parameter γ determines the anharmonicity and it is related to the frequency ω_y of a single-atom vibration in the normal direction by the relation

$$\omega_y^2 = 2\gamma^2 \varepsilon_d / m, \tag{2}$$

m being the atomic mass. Contrary to the parabolic potential studied previously,[9–12] the function (1) is nonconvex, i.e., it has an inflation point at $y = y_{\rm inf} \equiv \gamma^{-1} \ln 2$, so that $\omega_{\rm eff}^2(y) \equiv V_y''(y) > 0$ for $y < y_{\rm inf}$, but $\omega_{\rm eff}^2(y) < 0$ at $y > y_{\rm inf}$.

To model the substrate potential along the surface, we will use the function proposed by Peyrard and Remoissenet,[13]

$$V_x(x) = \frac{1}{2}\varepsilon_s \frac{(1+s)^2[1-\cos(2\pi x/a_s)]}{1+s^2-2s\cos(2\pi x/a_s)}. \tag{3}$$

Here, ε_s is the activation energy for diffusion of a single atom, a_s is the period of the substrate potential along the chain, and the parameter s ($|s| < 1$) describes the shape of the potential. The frequency ω_x of a single-atom vibration along the chain is connected to the shape parameter s by

$$\omega_x^2 = \omega_0^2 \left(\frac{1+s}{1-s}\right)^2 \quad \text{with} \quad \omega_0^2 \equiv \frac{2\pi^2 \varepsilon_s}{m a_s^2}. \tag{4}$$

In the following, we use a system of units where $a_s = 2\pi$, $\varepsilon_s = 2$, and $m = 1$, so that $\omega_0 = 1$.

The total potential energy of a single atom near the substrate is written as

$$V_{\rm sub}(x,y) = V_x(x) e^{-\gamma' y} + V_y(y). \tag{5}$$

The exponential factor in the first term of the right-hand side of Eq. (5) takes into account the decrease of the influence of the surface corrugation as the atoms move away from the surface, so that $V_{\rm sub}(x,y) \to \varepsilon_d$, when $y \to \infty$. Note that this factor is important because it results in a nonlinear mixing of x and y modes.

Thus, the substrate potential depends on four parameters: the adsorption energy ε_d, the frequencies ω_x and ω_y, and the coupling parameter γ'. In general, the former three parameters may be measured experimentally for a given adsystem. Considering the case of metal atoms adsorbed on a metal substrate such as, e.g., the Li-W(112) adsystem studied in Ref. 2 or the Li-Mo(112) system investigated in Ref. 3, in our calculations we will take $a_s = 2.73$ Å, which is the distance between the wells along a furrow on the W(112) surface, $\varepsilon_s \sim 0.1$ eV, $\varepsilon_d \sim 3$ eV, and $\omega_x \lesssim \omega_y \sim 10^3$ cm^{-1}, which are typical values for these systems.[1,14] Returning to our system of units and taking for the sake of concreteness $\omega_x = 1.5$ and $\omega_y = 2$, we get $\varepsilon_d = 60$, $\gamma = 0.183$, $y_{\rm inf} = 3.80$, and $s = 0.2$ (such a choice was discussed in Ref. 15) As for the parameter γ' which is not critical for the present study, we will take $\gamma' = 2\gamma = 0.366$ for the sake of concreteness.

As shown in Refs. 9–12, the transverse degree of freedom comes into play when the atoms start to use a repulsive branch of the interatomic interaction. In order to study our model qualitatively, let us first investigate the case of exponential interatomic repulsion,

$$V_{\rm int}(r) = V_0 \exp(-\beta_0 r), \tag{6}$$

where V_0 is the amplitude and β_0^{-1} determines the typical range of the interaction. In order to prevent the atoms from escaping to infinity as V_0 increases, we must impose $\beta_0 > \gamma$; we have chosen $\beta_0 = 2\gamma = 0.366$.

As discussed above, to study a realistic model, we have to take into account that the atoms attract each other at large distances. Consequently, to simulate the process of growth of the second layer, we have to add to the function (6) an attractive branch, so that the total interatomic potential will take the form

$$V_{\rm int}(r) = Ve^{-\beta r} - V'e^{-\beta' r}, \tag{7}$$

where $\beta' < \beta$ and $V' < V$. Adding to Eq. (7) an appropriate constant, the function (7) can be rewritten in a generalized Morse form as

$$V_{\rm int}(r) = \varepsilon_a \left\{ \frac{\beta'}{\beta - \beta'} e^{-\beta(r-r_a)} - \frac{\beta}{\beta-\beta'} e^{-\beta'(r-r_a)} \right\}, \tag{8}$$

where ε_a is the interatomic bonding energy of a molecule adsorbed on the surface, r_a is the molecule's equilibrium distance, and the exponents β and β' are related to the frequency ω_a of interatomic vibration by the relation

$$\omega_a^2 = \varepsilon_a \beta \beta'. \tag{9}$$

If we put $\beta' = \frac{1}{2}\beta$, the potential (8) reduces to the standard Morse form. Having in mind the application of our model to the lithium film, we have chosen $r_a \approx 3.04$ Å (the interatomic distance in lithium metal), or $r_a = 7$ in our system of units. The energy of interaction between two adsorbed metal atoms usually lies within an interval $\varepsilon_a \sim 0.1 - 0.5$ eV,[16] or $\varepsilon_a \sim 2 - 10$ in our system of units. We have chosen the value $\varepsilon_a = 6$ for the calculation presented below. As for the exponents β and β', the standard Morse choice, which works quite well for a free molecule, turns out to be inappropriate for the problem under investigation, because the chemically adsorbed atoms are partially ionized.[14] This reduces significantly the strength of the interatomic bond so that the attractive branch of the interatomic potential is much weaker than in a free molecule. On the other hand, the repulsive branch is significantly stronger than for a free molecule, because it is now caused by an overlap of atomic cores. This situation leads to a strong inequality $\beta' \ll \beta$, however these parameters are not easy to derive from experimental data. After several attempts, we have finally chosen $\beta = 1.9$ and $\beta' = 0.19$, which provide interesting results in agreement with experimental observations as discussed below. However, we cannot say categorically that this is the only parameter set which has this property. Moreover, our choice of parameters does not claim at a detailed quantitative interpretation of the experiments, because the model is still oversimplified for a real system of adatoms. In the spirit of the FK model, we have tried to design the minimal model able to describe the phenomena of interest, particularly the reconstruction of the growing crystal. This phenomenon involves a rather subtle balance between different interactions. This is why the "minimal model" has to be much more complicated than the standard FK model to capture these effects.

The main goal of the present work is to find the sequence of the ground state configurations when the concentration of atoms is increased, while all other model parameters are fixed. In order to control the coverage of adatoms, we impose periodic boundary conditions, taking a fixed number of minima of the substrate potential (we have used $M = 16$) and varying the number N of atoms (N was changed from 14 to 32). For each N the GS configuration as well as the nearest metastable states are searched for with a standard molecular-dynamics (MD) algorithm. Namely, we are starting from an appropriate initial configuration and allow the atoms to relax to a nearest minimum of the total potential energy of the system. Thus, the computer algorithm reduces to the solution of the equations of motion, which follow from the potentials (5) and (6) or (8) with an artificially introduced viscous friction.[17] As was explained in Refs. 10 and 11, for the model under investigation, we have to take into account the interaction of a given atom with all the other atoms. Obviously, in computer simulation, we can include only the interaction with a finite number of neighbors. Therefore, we have to introduce a cutoff distance r^* (we have chosen $r^* = 9.5a_s$) and account only for the interactions between the atoms separated by distances lower than r^* as usual in MD simulation.

Contrary to the case of the standard FK model for which, the appropriate initial configuration can be determined analytically although a complete solution cannot be obtained, guessing the "correct" initial configuration in the present study is difficult. The following methods help to find it. First, we start from the simpler model of the exponential interatomic interaction (6), and investigate its behavior when the amplitude V_0 of the repulsion increases. The knowledge of the phase diagram of this system is then used for the case of a Morse interaction. Second, we start from different "reasonable" initial configurations, and then compare the energies of the resulting final configurations. Finally, we use Langevin equations of motions instead of the Newtonian ones, i.e., we introduce some nonzero temperature T, which allows the system to overcome small barriers around a secondary minimum (we have used $T \sim 0.01$ in our energy units at the beginning of simulation). Then T is decreased slowly to zero in the final stage of the calculations. Although all these tricks cannot guarantee that we obtain the true GS configuration, they at least help to find it with a high probability.

III. REPULSIVE INTERATOMIC INTERACTION

A. The $\theta = 1$ case

Let us begin from the simplest case of the commensurate $\theta = 1$ structure with the exponential repulsion (6) between the atoms. As shown in Ref. 9, at small magnitude of the repulsion, $V_0 < V_{zz}$, the GS of the chain is trivial (TGS), because all atoms occupy the minima of $V_{\rm sub}(x,y)$, so that the atomic coordinates are simply $x_l = la_s$ and $y_l = 0$ ($l = 0, \pm 1, \ldots$). But with increasing V_0, at $V_0 = V_{zz}$ the TGS evolves into a zigzag ground state (ZGS), where nearest-neighboring atoms are shifted transversely in the opposite directions, so that they have the coordinates

$$x_l = la_s, \quad y_{2l} = y_+, \quad y_{2l+1} = -y_-, \quad l = 0, \pm 1, \ldots . \quad (10)$$

The critical repulsion V_{zz} can be obtained from a linear stability analysis of the trivial ground state.[9–11] An analysis restricted to nearest-neighbor interactions gives $a_s\omega_y^2 = -4V'_{\rm int}(a_s)$, so that for the exponential repulsion (6), we obtain

$$V_{zz} = (\omega_y^2 a_s/4\beta)\exp(\beta a_s). \quad (11)$$

With the parameters chosen above, Eq. (11) yields $V_{zz} \approx 171$.

For a parabolic transverse potential $V_y(y)$ the displacements are symmetric, $y_+ = y_- = y_0$; they increase when V_0 is raised above V_{zz}, and at some second critical value of V_0 the ZGS is transformed into a more complicated GS structure.[11] But for a nonconvex transverse potential such as the Morse potential (1), where $y_+ > y_0 > y_-$, the scenario may change if the displacement y_+ approaches to the inflection distance $y_{\rm inf}$, i.e., when $y_+ \lesssim y_{\rm inf}$. A qualitative understanding of the behavior of the system can be obtained by fixing all the atoms but one at the minima of the substrate potential, and considering the total potential energy as a function of the transverse displacement of the atom which is left free,

$$V(y) = V_y(y) + 2V_0 \sum_{l=1}^{\infty} e^{-\beta\sqrt{(la_s)^2+y^2}}. \quad (12)$$

It is easy to check that for small V_0 the function (12) has a single minimum at $y = 0$. For large V_0, it has a single minimum at some $y > 0$, but there exists an interval of V_0 values, $V_1 < V_0 < V_1'$, for which the function $V(y)$ has two minima simultaneously. Thus, with the increase of V_0, the chain can undergo a first-order phase transition, forcing out one of its atoms to a "second layer."

The scenario remains qualitatively the same if we take into account the displacements of other atoms and adjust their positions in the presence of the escaping atom, although the numerical values of V_1 and V_1' will, of course, be different. For the chosen parameters of the model, the numerical calculations give $V_1 \approx 152$ and $V_1' \approx 177$.

Let us denote this state with an escaping atom and the corresponding shift of its neighbors as the "second-layer" (sl) excitation. Now, we have a situation which was studied previously[18] for the FK model with nonconvex interatomic interaction. Let us introduce the energy of the sl excitation as

$$\varepsilon_{\rm sl} = E_1 - E_0, \quad (13)$$

where E_0 is the energy of the trivial or zigzag GS and E_1 is that for the configuration with one escaped atom. The dependence of $\varepsilon_{\rm sl}$ on V_0 is plotted in Fig. 1 which shows that, below some critical value of the repulsion, $V_0 < V_{\rm crit}^{(1)}$ (for our choice of parameters $V_{\rm crit}^{(1)} \approx 162$), the energy of the sl excitation is positive, so that the sl configuration corresponds to a metastable state. On the other hand, for $V_0 > V_{\rm crit}^{(1)}$, the energy of creation of the sl excitation becomes negative, and the system might tend to create as many escaped atoms as possible. But because two escaped atoms repel each other according to an exponential law,

$$V_{ll}(r) \approx V_{\rm sl} e^{-\beta_{\rm sl} r}, \quad (14)$$

where $\beta_{\rm sl} \sim \beta_0$ and $V_{\rm sl} \gtrsim V_0$, the escaping of new atoms will finally be suppressed. The density of sl excitations (i.e., the atoms in the "second layer") is determined by the competition between the energy gain (13), due to the negative creation energy of the sl excitation and the energy loss owing to positive energy (14) of repulsion of the sl excitations. The period $a_{\rm sl}$ of the sl structure follows from the equation $V_{ll}(a_{\rm sl}) + \varepsilon_{\rm sl} = 0$, or

$$a_{\rm sl} \approx -\beta_{\rm sl}^{-1} \ln(-\varepsilon_{\rm sl}/V_{\rm sl}). \quad (15)$$

This analysis shows that, with increasing V_0, at $V_0 = V_{\rm crit}^{(1)}$, the system with exponential interatomic repulsion undergoes a first-order phase transition from the trivial (or zigzag) ground state to the configuration with "escaped" atoms, and then an infinite series of second-order phase transitions, in which the period of the sl superstructure decreases from infinity to $2a_s$ (so that the coverage θ_2 of atoms in the second layer increases from 0 to 1/2).

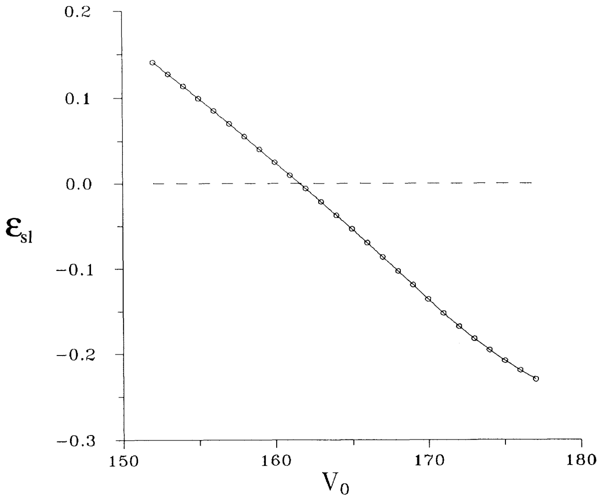

FIG. 1. The energy of the "second-layer" excitation $\varepsilon_{\rm sl}$ versus V_0.

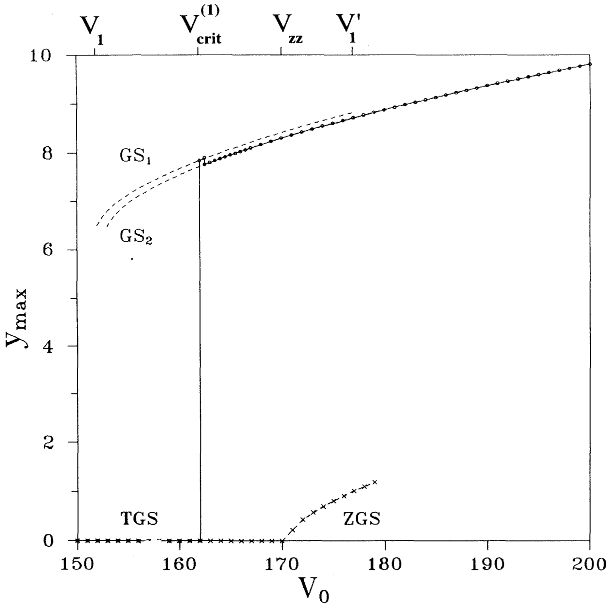

FIG. 2. The maximal transverse atomic displacement as a function of V_0 for the model with exponential interatomic repulsion. GS_n corresponds to the configuration with $\theta_2 = n/16$, so that the period of the superstructure of "escaped" atoms is $a_{sl} = 16a_s/n$. Full curves correspond to the ground state configurations, and broken curves correspond to metastable states.

The results of the numerical calculations are presented in Fig. 2, where we have shown the maximum atomic displacements in the transverse direction as a function of V_0. Because of the finite size of the model system (16 atoms), the first state that we can observe corresponds to $\theta_2 = 1/16$, and then $\theta_n = n/16$ could, in principle, be found. In the parameter range that we have investigated, we have observed only the transitions from the TGS to the superstructure with $\theta_2 = 1/16$ ($a_{sl} = 16a_s$), then to the structure with $\theta_2 = 1/8$ ($a_{sl} = 8a_s$), then with $\theta_2 = 3/16$ (this structure is not perfect because 3 and 16 have no common divisors), and then to $\theta_2 = 1/4$ ($a_{sl} = 4a_s$).

B. The $\theta > 1$ case

In order to understand crystal growth on a surface, we must investigate now the properties of the system with increasing atomic coverage. Let us first consider the simplest situation where we have added one extra atom to the $\theta = 1$ coverage, i.e., $\theta = 17/16$ for our system with 16 potential wells.

For the standard FK model with only one degree of freedom, the extra atom has no other choice but lying in line with the others. Due to the periodic substrate potential, the atoms do not distribute evenly on the available length. On the contrary, the FK model exhibits in this case a localized defect, where one well is occupied by two atoms, and the atoms in the neighboring wells are slightly disturbed from their equilibrium position. This is the so called dislocation or kink.[6] When the interatomic interaction is very strong, this defect disturbs the atoms over many lattice spacings and can be described in the continuum limit as a soliton of the sine-Gordon model. In this extreme case, the defect can move freely in the lattice. For narrower defects, which is the case for crystal growth, the kink has some minimum-energy configuration which can be either with two particles situated symmetrically in one well (i.e., the center of the kink lying in the middle between two sites $X_C = 1/2$) or with one particle exactly on the top of the potential (i.e., the center of the kink being exactly on one particle, $X_C = 0$). For the sinusoidal potential ($s = 0$), the minimum energy configuration corresponds to the case $X_C = 1/2$. When s deviates from 0, the case $X_C = 0$ may become favorable,[13] and when the interatomic interaction increases, the favorable kink position is alternatively $X_C = 0$ and $X_C = 1/2$.

This well known picture for the standard FK model may not be correct for crystal growth, where the extra atoms have the freedom to start forming a second layer. This is the situation that we want to investigate in this section with our generalized FK model.

The kink structure for the generalized FK model with the parabolic transverse potential was studied in. Ref. 10. In this case with increasing V_0, at a critical threshold $V_0 = V_{zz}^{(k)}$ ($V_{zz}^{(k)} < V_{zz}$), the atoms in the kink region create a zigzag structure, while the atoms far from the kink region remains in the TGS. With further increase of V_0, the transversal atomic displacements increase too, and at $V_0 > V_{zz}$, when the background structure changes to the ZGS, the atomic displacements in the kink region are still the largest. (Note that in the ZGS there exist two kinds of kinks, the so-called "massive" and "nonmassive" ones.[10] But this is not important for the problem under investigation; in the present study we are interested in the "massive" kinks only.) Similarly to the scenario described above for the $\theta = 1$ case, one of the atoms, namely, the one with the maximum transversal coordinate, may escape to the second layer at some $V_0 = V_k$, when this coordinate becomes close to the inflection point $y_{\rm inf}$. Such a configuration can be designated as the (k+sl) configuration, because it involves simultaneously a kink and the formation of the second layer. It is metastable within the interval $V_k < V_0 < V_{\rm crit}^{(k)}$, and becomes the minimum-energy configuration for $V_{\rm crit}^{(k)} < V_0 < V_k'$. For our choice of parameters we have found $V_k \approx 47$, $V_k' \approx 175$, and $V_{\rm crit}^{(k)} \approx 68$.

The scenario looks similar to the one that we described for the $\theta = 1$ coverage: the generalized FK allows the formation of a second layer of atoms. The main difference lies, however, in the magnitude of atomic repulsion, which is necessary to form this layer. It is significantly decreased in the presence of extra atoms ($V_k \approx 47$ instead of $V_1 \approx 152$), because those atoms contribute to the formation of kinks in the core of which particles escape more easily. The same picture holds for coverages higher than 17/16. More generally, for $\theta > 1$, in the standard FK model the ground state consists of an array of kinks with a density that increases with θ. In the generalized FK model with a nonconvex potential in the transverse direction, each kink acts as a nucleation site for the formation of the second layer, because it evolves into a (k+sl) configuration when V_0 increases. These transitions occur one by one through an infinite series of superstructures within a narrow interval of V_0 values, and stop at some point $V_0 = V_{\rm crit}^{(\theta)}$ ($V_{\rm crit}^{(\theta)} < V_{\rm crit}^{(k)}$). The physics of the resulting structure is quite clear: when the interatomic repulsion is large enough, the extra atoms prefer to occupy the second layer.

Then, with further increase of V_0, at some $V_0 = V_2$ the atoms belonging to the background of the first layer start to escape and form sl excitations. Because these excitations repel each other, these new escaped atoms emerge just in the middle between the kinks. Such a configuration is metastable in a range $V_2 < V_0 < V_{\rm crit}^{(2)}$, and then corresponds to the minimum-energy configuration at $V_{\rm crit}^{(2)} < V_0 < V_2'$. We have checked this scenario numerically for $\theta = 18/16$ and found that the value V_2 for which atoms in the background start to escape is $V_2 \approx 148$ and these excitations become stable for $V_{\rm crit}^{(2)} \approx 159$. The results are shown in Fig. 3. These values should be compared with the values $V_1 \approx 152$ and $V_{\rm crit}^{(1)} \approx 162$ found for the $\theta = 1$ coverage. They are lower because, for $\theta > 1$ the presence of the extra atoms induces the formation of kinks, which not only promote the escaping of atoms in their core, but also modify the background state.

These results are interesting because they illustrate some subtle effects in surface growth. Consider a system such that the magnitude of the interatomic repulsion is in the range $V_{\rm crit}^{(2)} < V_0 < V_{\rm crit}^{(1)}$, and assume that θ is increased regularly by atomic deposition to grow new layers on the surface. For $\theta = 1$, the minimum-energy configuration corresponds to having all the atoms in the first layer ($\theta_1 = 1$, $\theta_2 = 0$), because $V_0 < V_{\rm crit}^{(1)}$. For $\theta = 17/16$, $\theta_1 = 1$ and $\theta_2 = 1/16$, i.e., the extra atom has formed a second layer. But if one more atom is added by going to $\theta = 18/16$, the minimum-energy configuration is achieved for $\theta_1 = 14/16$ and $\theta_2 = 4/16$, i.e., *the addition of one atom has induced the extraction of two atoms from the first layer.* This reconstruction effect is indeed very sensitive to the choice of interatomic potentials, but this is not surprising because it is a usual property of structural transformation. It is interesting that the generalized FK model with a nonconvex transverse potential, although it is still rather simple, can show such a phenomenon.

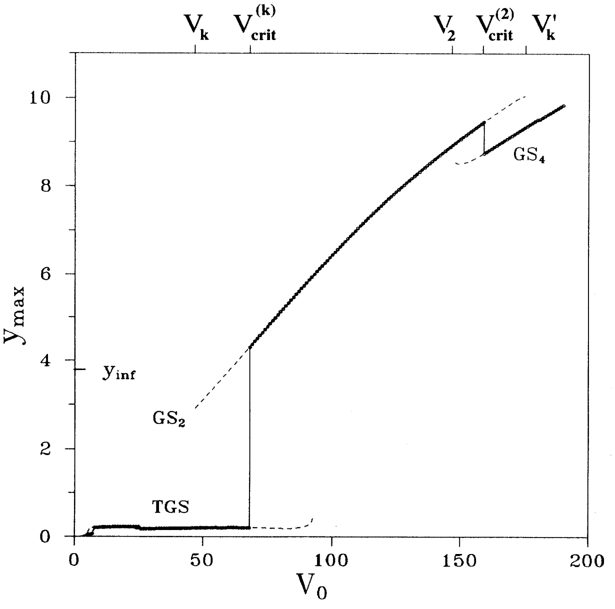

FIG. 3. The same as Fig. 2 for $\theta = 18/16$. GS$_2$ corresponds to the configuration with two (k+sl) excitations, and GS$_4$, to four "escaped" atoms, or the ($2k$+4sl) configuration.

IV. THE MORSE INTERATOMIC POTENTIAL

Let us now consider the more realistic case of a generalized Morse interaction (8) between the atoms. As mentioned above, the model parameters $\beta = 1.9$ and $\beta' = 0.19$, which can only be roughly estimated from available data, have been selected to provide qualitative agreement with experiments. We have been helped, in this selection, by the understanding obtained from the simpler case of a purely repulsive interaction described in the previous section.

The mechanism of surface growth has been investigated by chosing a given interaction potential and varying the coverage. As before, we consider a system with $M = 16$ minima of the substrate potential. The number of adatoms has been varied from $N = 16$ to $N = 32$ in order to get coverages in the range $1 \leq \theta \leq 2$. For each coverage, we have been looking for the absolute minimum or local minima of the energy in order to determine the stable ground state and possible metastable states. As the study of the previous section has shown that the stable or metastable states are not always the states with a maximum number of atoms in the first layer, we have considered in each case several initial configurations for the relaxation. The first initial condition assumes simply a full coverage of the first layer, i.e., M atoms in the first layer and $N - M$ in the second layer. A second initial state puts only $M - 1$ atoms in the first layer, giving a partial coverage $\theta_1 = (M - 1)/M$, and the others $N - M + 1$ atoms in the second layer. We also started from $M - 2$ or $M + 1$ atoms in the first layer.

The numerical calculations exhibit some interesting features of the epitaxial growth. For high overall coverage $\theta = N/M$ with $N \geq 22$, all the initial states converge to the *same* final configuration, which corresponds to a completely filled first layer ($\theta_1 = 1$). At lower coverages ($16 \leq N \leq 21$), there exist *two stable final configurations.* They are shown in Fig. 4. The first class of configurations (a–f in Fig. 4) have a full coverage of the first layer (16 atoms), while the second class of configurations (g–l in Fig. 4) has only 15 atoms in the first layer ($\theta_1 = 15/16 = 0.94$). We did not find any stable configuration with less than 15 or more than 16 atoms in the first layer. Figure 5 shows the energies of the two sets of configurations found in the range $16 \leq N \leq 21$. For the lowest coverages $N = 16$ and $N = 17$, the ground state configuration corresponds to a completely filled first layer ($\theta_1 = 1$), but in the range $18 \leq N \leq 21$ it is, on the contrary, the partially filled first layer ($\theta_1 = 15/16$) which is the most stable, i.e., the configuration in which the first layer has an empty site (antikink).

Thus, the model exhibits the reconstructive growth scenario that we had foreseen in the simpler case of a purely repulsive interaction. At $\theta \leq 1$, the incoming atoms fill the first layer. In the interval $1 \leq \theta \lesssim 1.1$, new incoming atoms occupy the second layer. Then, within the interval $1.1 \lesssim \theta \lesssim 1.35$, the incoming atoms continue to fill the second layer but, at the same time, they stimulate the escaping of atoms from the underlying first layer to the second layer, causing the reconstruction of the structure of the growing film. Finally, for $1.35 \lesssim \theta \leq 2$, the escaped atoms are pulled back to the first layer, and the film continues to grow in a usual way, new incoming atoms being placed over the completely filled first layer.

To describe the atomic structure of the second layer, we have to recall that two kinks in the FK model interact by two mechanisms.[17] First, there is always an "indirect" kink-kink interaction. This interaction is due to the disturbance of the background chain caused by a kink. This perturbation, which decays away from the center of a kink, is felt by the second kink. The "indirect" interaction is always repulsive (at least for a convex interatomic interaction) and may be approximately described by an exponential law $V_{\text{indirect}}(r) \propto \exp(-r/d)$ as $r \to \infty$,[19] where d is the kink width (i.e., d measures the extension of the region perturbed by the kink). In fact, the "indirect" interaction is nothing else than the usual elastic interaction between two local defects. In a one-dimensional FK model, this interaction is exponential and can be estimated from the continuum limit because it corresponds then to the soliton-soliton interaction of the sine-Gordon model. In a real three-dimensional model, the interaction between defects decreases according to the dipolar law $V_{\text{indirect}}(r) \propto r^{-3}$.[20,21] Second, if we take into account the interaction between all the atoms of the chain, which is the realistic situation, there always exists a "direct" kink-kink interaction, simply because each kink contains one extra atom, and these atoms interact according to the potential $V_{\text{int}}(r)$. Thus, the total kink-kink interaction is a superposition (approximately a sum) of the "direct" and "indirect" interactions. For the model with exponential interatomic repulsion (6), the two contributions of the kink-kink interaction are repulsive so that the total interaction is indeed repulsive. Consequently, the atoms in the second layer tend to fill it uniformly, creating a superstructure with an interatomic distance that is as large

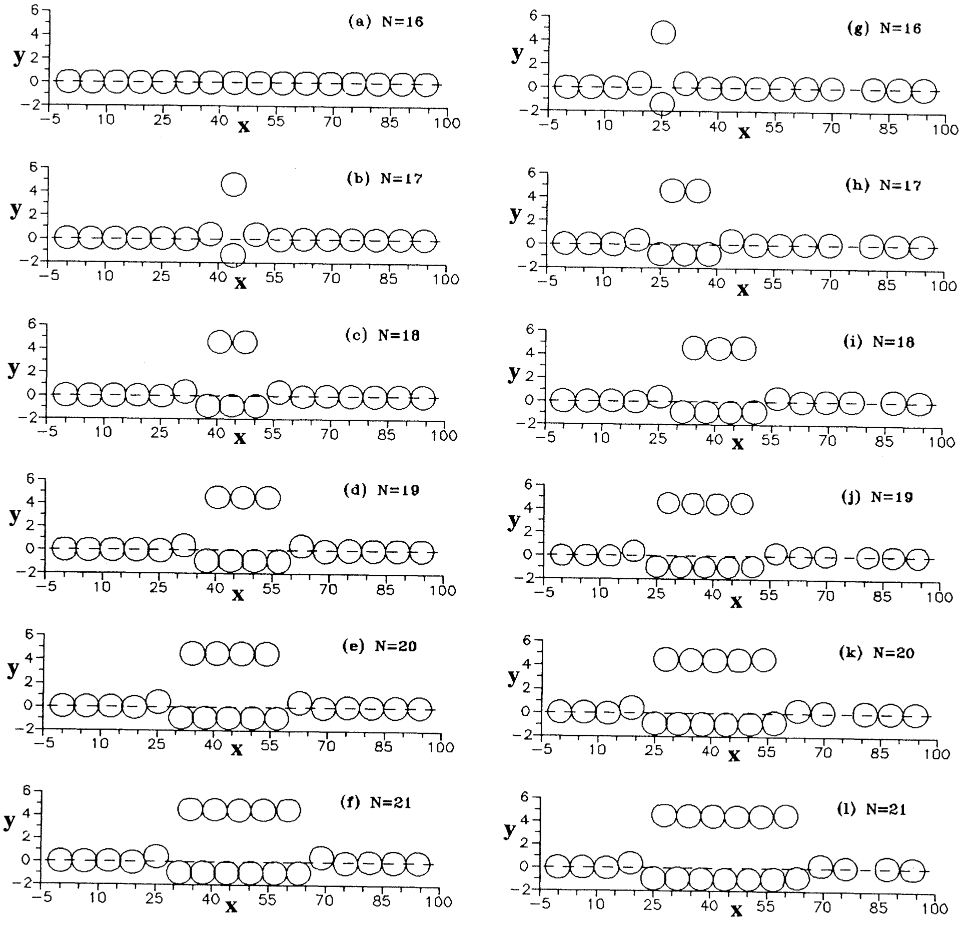

FIG. 4. Atomic configurations for the model with the generalized-Morse interaction (8). $M = 16$, $r_a = 7$, $\varepsilon_a = 6$, $\beta = 1.9$, and $\beta' = 0.19$. The number of substrate potential minima is $M = 16$, the coverage is $\theta = N/M$ and is increased by increasing the number N of adatoms from 16 to 21. In this range of coverage, for each N, the system has two stable configurations: the first ones (a–f) are obtained with a full coverage of 16 atoms in the first layer, while the second class of configurations (g–l) has only 15 atoms in the first layer.

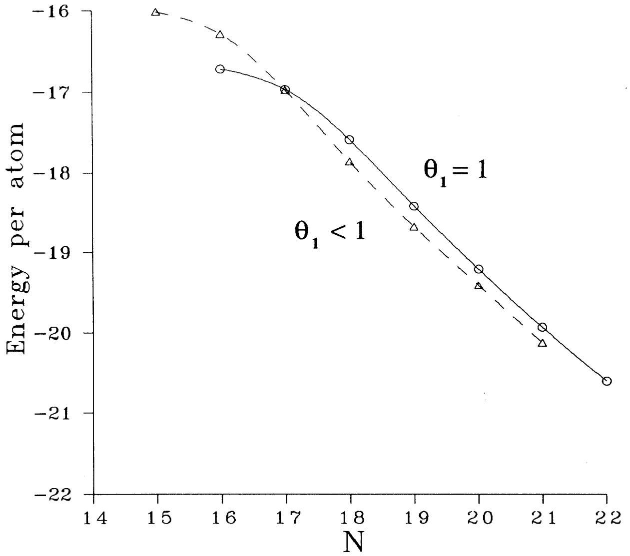

FIG. 5. The energy per atom E/N versus N for the configurations of Fig. 4. The points connected by the full curve correspond to the $\theta_1 = 1$ case (the configurations a–f in Fig. 4), and the points connected by the broken curve, to the $\theta_1 = 15/16$ configurations (the configurations g–l in Fig. 4).

as possible. However, for the model with the Morse interatomic potential (8) that we consider here, the total kink-kink interaction at distances larger than the equilibrium distance r_a of the Morse potential, $r > r_a$, is the result of a competition between the "indirect" kink-kink repulsion and a "direct" attraction. Thus, depending on the parameters of the model, the resulting interaction between the atoms in the second layer may or may not have a minimum. It is clear that if a minimum exists at some distance r_k, the atoms in the second layer will tend to be organized into clusters (islands) with a mean interatomic distance close to r_k. For our choice of parameters, the kink-kink total interaction potential has a minimum for $r_k \gtrsim r_a$ and this explains the formation of the clusters in the second layer as shown in Fig. 4. It is important to notice that this formation of clusters, often observed in experiments, is made possible by the attractive branch of the interatomic potential. It would not have been possible with the simpler model studied in Sec. III.

Besides the reconstructive growth, the generalized FK model studied here exhibits two other interesting phenomena. The first is connected with the exponential factor $\exp(-\gamma' y)$ in the right-hand side of Eq. (5). As this term introduces a coupling between the x and y displacements, the atoms in the first monolayer, which are displaced from the minima of the substrate potential in the x direction, should additionally be forced in the transversal direction. It is easy to see that if an atom is shifted by Δx ($\Delta x \lesssim \pi$) along the chain from the corresponding minimum of $V_{\text{sub}}(x,y)$, at the same time it is submitted to a force in the y direction, which shifts it in the normal direction of the quantity,

$$\Delta y \approx \frac{1}{2}\gamma' \left(\frac{\omega_x}{\omega_y}\right)^2 (\Delta x)^2. \tag{16}$$

As a result, a submonolayer structure ($\theta < 1$), which may be considered as an antikink superstructure with the period $a_s/(1-\theta)$, should be corrugated in the normal direction with the same period as is shown in Fig. 6. Although this effect is quite trivial, it would be interesting to observe it experimentally with, e.g., the STM technique, because the amplitude of corrugation gives the value of the coupling parameter γ'.

The second effect has been observed, when we were studying the $\theta = 17/16$ atomic configurations as the parameter r_a of the generalized Morse potential (8) was varied within the interval $5.7 \leq r_a \leq 7$. As described above, for each value of r_a, we started from two different initial configurations: the first with $\theta_1 = 1$ and $\theta_2 = 1/16$ (one atom in the second layer), and the second with $\theta_1 = 17/16$ and $\theta_2 = 0$ (all atoms in the first layer). Calculations show that the $\theta_1 = 1$ final configuration always corresponds to the GS, but within the interval $6.1 \lesssim r_a \lesssim 6.6$ the $\theta_1 = 17/16$ configuration (i.e., with a kink into the first atomic layer, see Fig. 7) exists also as a metastable configuration. The energies of these two configurations as functions of r_a are plotted in Fig. 8. If we denote by ΔE the difference in energies of these two configurations, then at a nonzero temperature T the concentration of kinks in the first layer (owing to insertion of atoms from the second layer) may be estimated as $\theta_k \approx \theta_2 \exp(-\Delta E/k_B T)$, where $\theta_2 = 1/16$ for our case. This situation could have significant physical consequences, because previous investigations[10] of the zigzag-FK model have shown that a kink in the first layer is usually much more mobile [i.e., its motion is characterized by a lower activation (Peierls-Nabarro) barrier] than a kink in the second layer. Thus, if D_2 is the diffusion coefficient for the atomic motion in the second layer, i.e., for atoms moving over the filled first layer and D_k is the kink diffusion coefficient in the first layer, the average chemical diffusion coefficient can be estimated as

$$D = (D_2\theta_2 + D_k\theta_k)/(\theta_2 + \theta_k), \tag{17}$$

and in the case of $D_k \gg D_2$ and $\Delta E \sim k_B T$, we will have $D \gg D_2$. It is interesting that such a diffusion mechanism in which an atom from the second layer penetrates

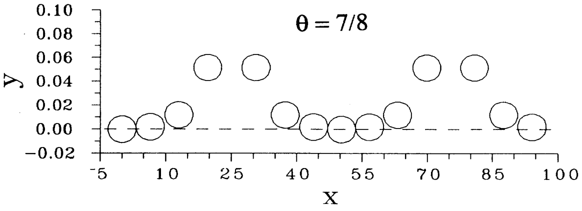

FIG. 6. The corrugated atomic structure for $\theta = 7/8 = 0.875$. Notice that the displacements in the y direction have been exaggerated to show clearly the corrugation.

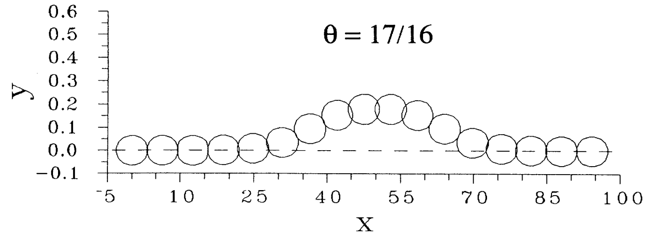

FIG. 7. A metastable configuration with one atom inserted into the first layer. $\theta = 17/16$, $r_a = 6.3$, $\varepsilon_a = 6$, $\beta = 1.9$, and $\beta' = 0.19$.

into the first layer and forms there a kink, which then runs for a large distance before an atom from the kink region will escape back to the second layer, was recently observed in a full molecular dynamics simulation.[22]

V. DISCUSSION

Because the model studied in the present work is characterized by a large number of parameters, we have tried to choose them in an appropriate way to describe real physical objects, for example, a lithium film adsorbed on the furrowed (112) surface of tungsten or molybdenum, which were studied experimentally in Refs. 2 and 3. However, we must be careful in drawing conclusions regarding the experiments, because the model is still oversimplified. First, the parameters of an interaction potential of chemically adsorbed atoms depend significantly on the distance between the atoms (owing to their mutual depolarization), as well as on the distance from an adatom to the surface (i.e., the parameters for the first adsorbed layer have to be distinguished from those for the second layer) and, moreover, in a general case the interaction has a much more complicated form than the sum of two exponential functions (8). In particular, the interaction can be anisotropic.[16] Second, in a realistic model the atoms have to have three degrees of freedom and the growing layers have to form two-dimensional arrays of atoms. Consequently, the model studied in the present work cannot claim to reach a detailed agreement with the experiments.[2,3] However, *the present model does predict effects that may explain the experimental results mentioned above.* Further theoretical investigations should be based on two-dimensional models, but the understanding gained in the present work might be helpful in studying these models. The model that we have considered here can be considered as a minimal model in the sense that all its characteristics are necessary to describe typical experimental results in epitaxial growth.

(i) We need to consider at least one displacement along the surface and one orthogonal to the surface, hence the x and y coordinates.

(ii) We must introduce the periodic potential, due to the atoms of the surface, as well as the potential in the transverse direction, which is responsible for the adsorption of the adatoms, hence the substrate potential (5).

(iii) The transverse potential must be nonconvex in order to observe atoms escaping from the first layer, allowing reconstructive growth.

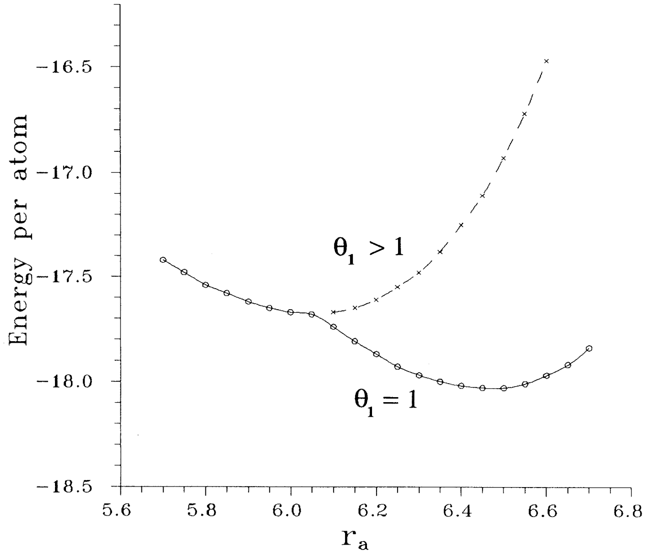

FIG. 8. The energies of the GS $\theta_1 = 1$ configuration (full curve) and the metastable $\theta_1 = 17/16$ configuration (broken curve) as functions of r_a. $\theta = 17/16$, $\varepsilon_a = 6$, $\beta = 1.9$, and $\beta' = 0.19$.

(iv) Finally, the interatomic potential must include both a repulsive part to limit the coverage of the first layer, and an attractive part to allow the formation of atomic clusters in the second layer.

In spite of the limitations of a minimal model, the present work has shown that for a certain (but realistic) choice of the parameters, the generalized Frenkel-Kontorova model with a nonconvex transversal degree of freedom describes reconstructive crystal growth. The calculations have shown, in particular, that the sequence of the ground state configurations, when the coverage θ increases above the value $\theta = 1$ exhibits a "sl-excitation-stimulated" first-order phase transition, so that at $\theta < \theta'$ and at $\theta > \theta''$ the GS configuration corresponds to a completely filled first layer, while within the interval $\theta' < \theta < \theta''$ (where $\theta' > 1$, but $\theta'' < 2$), the GS structure corresponds to a partially filled first layer. Such a sequence of structures of adsorbed atoms was observed in the experiments (Refs. 2 and 3), for the lithium film on the furrowed (112) surface of tungsten and molybdenum correspondently. Besides, the model studied above also predicts that a submonolayer film at $\theta \lesssim 1$ should be corrugated. This effect may be checked by the STM technique.

Finally, for a certain choice of the parameters, the model investigated in the present work describes a new diffusion mechanism, the "complicated exchange-mediated diffusion mechanism," which has been recently discovered in molecular-dynamics simulations of the Cu-Cu(100) adsystem.[22]

ACKNOWLEDGMENTS

This work was supported in part by the NATO Linkage Grant No. LG 930236. One of us (O.B.) was partially supported by the Soros Grants and by the Grant of the Ukrainian State Committee for Science and Technology. O.B. is indebted to V. K. Medvedev for discussion of the experimental results and to E. Majerníková and G. Drobný for hospitality at the Institute of Physics of the Slovak Academy of Sciences, where the final part of the simulations has been done. M.P. thanks the Institute of Physics of Kiev for its kind hospitality during the completion of this paper.

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