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ADIABATIC MOTION OF AN ATOMIC CHAIN IN PERIODIC POTENTIAL

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The adiabatic motion of a finite chain of atoms interacting in accordance with next-neighbour harmonic forces and placed in a periodic external potential (the Frenkel–Kontorova model) is investigated. The conditions are determined where the activation energy of the chain motion is lower than that of the motion of a single atom. The results are used to explain some experimental data on surface diffusion in chemisorbed systems.

1. Introduction

The coordinated motion of particles always plays an important role in the dynamics of systems consisting of interacting particles . The well-known Frenkel–Kontorova (FK) model [1] is one of those which adequately explain such a collective motion. The FK model describes a chain of harmonically interacting atoms in an external sinusoidal potential, so that the potential energy of the system is equal to

$$V=\tfrac{1}{2}g\sum_{i=2}^{N}\left(x_i-x_{i-1}-a\right)^2+\tfrac{1}{2}\epsilon_s\sum_{i=1}^{N}\left[1-\cos\left(\frac{2\pi x_i}{a_s}\right)\right]. \tag{1.1}$$

Here N is the total number of the atoms, x_i is the position of the ith particle, g is the elastic constant of the chain, a is the equilibrium distance for the interatomic potential, ϵ_s and a_s are the amplitude and the period of the external potential respectively. Further we will use the system of units with $\epsilon_s=2$, $a_s=2\pi$ and $m_a=1$, m_a being the mass of atoms. The FK model is successfully used to explain the motion of dislocations in crystals, the dynamics of planar domain walls in magnetic systems, the charge-density waves in quasi-one-dimensional conductors etc. (see, e.g. ref. [2]), and to describe the "solitonic" diffusion in a two-dimensional layer of atoms adsorbed on a crystal surface (see ref. [3]).

The FK model for an infinite atomic chain was investigated in a number of studies (see, e.g., refs. [4–10]). In the continuum approximation, long-wave excitations of the model are described by the exactly integrable Sine-Gordon (SG) equation [2]. As a result, the model admits topologically stable nonlinear solutions, so-called kinks. In the cases of $g<\infty$ or $N<\infty$ the FK model admits kink solutions too (note that the terms misfit dislocations, topological solitons, and crowd-ions are also used by some authors). However, in these cases the model is nonintegrable, and, in particular, the motion of kinks occurs in the periodic Peierls–Nabarro potential whose amplitude, ϵ_p, is much lower than that of the external potential, ϵ_s. Moreover, the effective mass of a kink, m, is also lower than those of the chain atoms, m_a. Both these properties ($m \ll m_a$ and $\epsilon_p \ll \epsilon_s$) result in the fact that kinks play an important role in the FK model dynamics.

If the interparticle potential has an attractive branch, then a finite chain of N atoms can also exist. Naturally, the question of the mobility of such clusters arises. In particular, this problem is very important for the description of surface diffusion of adsorbed atoms or molecules [3]. It is easy to understand that the mobility of clusters is mainly determined by the ratio between the period

a_s and the equilibrium distance a. For example, the positions of atoms which are rigidly coupled in the chain ($g = \infty$) may be presented as follows:

$$x_j = ja + X/N - (N+1)a/2, \tag{1.2}$$

where

$$X = \sum_{i=1}^{N} x_i, \tag{1.3}$$

and the potential energy of the chain is described by the expression

$$\epsilon(X) = N - \sum_{j=1}^{N} \cos x_j = N - \frac{\sin(Na/2)}{\sin(a/2)} \cos(X/N), \tag{1.4}$$

so that the activation energy for the chain's motion is equal to

$$\epsilon_a = 2\,|\sin(Na/2)|/\sin(a/2). \tag{1.5}$$

Therefore it follows that the maximum value of ϵ_a is reached for the commensurate case ($a = 2\pi$) and is equal to $\epsilon_a = 2N$, and the minimum values are equal to zero and are achieved at $a = a_n^\infty$, where

$$a_n^\infty = 2\pi - n(2\pi/N),\ n = 1, 2, \ldots, \mathrm{int}(N/2). \tag{1.6}$$

The behaviour of the finite FK chain was studied in refs. [11–14]. All equilibrium states of the FK chain for some fixed parameters of the model were obtained numerically by Markov and Karaivanov [12]. It was found that the activation energy ϵ_a versus the number of atoms N oscillates around a nearly constant value which is lower than that for a single atom if the natural misfit is greater than the critical misfit, above which misfit dislocations can be spontaneously introduced at the free ends.The present work develops ideas of ref. [12]. We determine the ground and stationary states of the FK chain as well as examine in detail its adiabatic (i.e. infinitely slow) motion for arbitrary parameters of the system. Our main interest is to determine the system parameters under which the mobility of the N-cluster is sufficiently high. The paper is organized as follows. In section 2 we describe the model, introduce the parameters of the chain's motion, and present the algorithm of the computer program designed for calculating these parameters. In section 3 we present the results of the calculations, and in section 4 we interpret these results using the "solitonic" terminology. The limitations and possible generalizations of the model are considered in section 5. In section 6 we discuss the way in which the FK model can be applied to describe the surface diffusion of adparticles. Finally, in section 7 we give brief conclusions.

2. Model and computer program

The model (1.1) is characterized by three parameters: N, g, and a. Note that it is sufficient only to consider the parameter a within the interval $\pi \leqslant a \leqslant 2\pi$, since the potential energy (1.1) is not changed provided the transformation of the equilibrium distance, $a \to \pm a + 2\pi$, and the positions of the atoms, $x_j \to \pm x_j + 2\pi j$, are done simultaneously.

The stationary-state configurations of the chain follow from solutions of the system of equations

$$\partial V/\partial x_i = 0, \quad i = 1, 2, \ldots, N. \tag{2.1}$$

The method of computerized solution of this system was described by Snyman and van der Merwe [15].

To classify various solutions $\{x_i^{(0)}\}$ of the system (2.1), it is necessary to find, as usual, eigenvalues λ_n of the elastic matrix $\boldsymbol{A} \equiv \{A_{ij}\}$, $A_{ij} = \partial^2 V/\partial x_i\, \partial x_j\,|_{x_i = x_i^0}$:

$$\boldsymbol{A}\boldsymbol{u}^{(n)} = \lambda_n \boldsymbol{u}^{(n)}, \tag{2.2}$$

where $\boldsymbol{u}$ is the N-dimensional vector: $\boldsymbol{u} = \{u_i\}$, and $u_i = x_i - x_i^{(0)}$ is the atomic displacement away from the stationary state. The symmetric matrix $\boldsymbol{A}$ can be reduced to a diagonal form with the help of an unitary matrix $\boldsymbol{T}$:

$$\boldsymbol{A} = \boldsymbol{T}\boldsymbol{B}\boldsymbol{T}^{-1},\ \boldsymbol{B} \equiv \{B_{mn}\},\ B_{mn} = \lambda_n \delta_{mn}, \tag{2.3}$$

$$\boldsymbol{u}^{(n)} = \boldsymbol{T}\boldsymbol{v}^{(n)},\ \boldsymbol{v}^{(n)} \equiv \{v_m^{(n)}\},\ v_m^{(n)} = v_n \delta_{mn}. \tag{2.4}$$

Then, close to a stationary state, the potential energy of the chain converts into the canonical form:

$$V = \mathrm{const}(x_i^{(0)}) + \tfrac{1}{2} \sum_{n=1}^{N} \lambda_n v_n^2. \tag{2.5}$$

From the physical viewpoint, only the following stationary states are of interest: the minima of the potential energy ($\lambda_n > 0$ for all n), and the saddle points with one eigenvalue being negative, and others, positive ($\lambda_1 < 0 < \lambda_2 < \ldots < \lambda_N$). The neighbouring local minima can always be connected by a "saddle" trajectory, i.e. by a curve which passes through the saddle point and is determined by the solution of the following system of differential equations:

$$\partial x_i/\partial\tau = -\partial V/\partial x_i, \quad i = 1, 2, \ldots, N, \tag{2.6}$$

where τ is a parameter along the trajectory. The saddle trajectory is the curve of steepest descent; at the stationary points the direction of the saddle trajectory is defined by the eigenvector $\pm\boldsymbol{u}^{(1)}$ corresponding to the minimum eigenvalue λ_1.

The stationary state of the system with the lowest value of potential energy is called the ground state. Evidently, the ground state of a finite FK chain is infinitely degenerated since the substitution $x_i \to x_i + 2\pi$ transfers one ground state to the neighbouring one. We will call the "adiabatic" trajectory the saddle trajectory which connects the neighbouring ground states of the system. Every state of the system on the adiabatic trajectory can be associated with a unique parameter, the coordinate X, defined by (1.3) according to Bergmann and coworkers [16]. Thus, the potential energy of the system is described by the function

$$\epsilon(X) = V(\{x_i\})\,|_{\{x_i\}\in\text{adiab.tr.}}, \tag{2.7}$$

which is periodic with the period

$$b = 2\pi N. \tag{2.8}$$

If two ground states can be connected by several different saddle trajectories, the trajectory with the minimum value of activation energy, ϵ_a, defined by the relationship

$$\epsilon_a = \max[\epsilon(X)] - \min[\epsilon(X)], \tag{2.9}$$

should be taken as the adiabatic trajectory.

As the system moves along the adiabatic trajectory, the kinetic energy of the chain, $K = \frac{1}{2}m_a\Sigma_{i=1}^{N}(\partial x_i/\partial t)^2$, takes the form

$$K = \tfrac{1}{2}m_a \sum_{i=1}^{N}\left(\frac{\partial x_i}{\partial X}\frac{\partial X}{\partial t}\right)^2 = \tfrac{1}{2}m\left(\frac{\partial X}{\partial t}\right)^2, \tag{2.10}$$

where an effective mass of the chain is equal to (see ref. [10])

$$m(X) = m_a \sum_{i=1}^{N}(\partial x_i/\partial X)^2. \tag{2.11}$$

Using eqs. (1.3) and (2.6), the expression (2.11) can be rewritten in the form:

$$m = \sum_{i=1}^{N}\left\langle\frac{\partial x_i/\partial\tau}{\partial X/\partial\tau}\right\rangle^2 = \left.\frac{\sum_{i=1}^{N}(\partial V/\partial x_i)^2}{\left(\sum_{i=1}^{N}\partial X/\partial x_i\right)^2}\right|_{\{x_i\}\in\text{adiab.tr.}} \tag{2.12}$$

Taking into account the following relationship for the stationary state,

$$\left.\frac{\partial V}{\partial x_i}\right|_{\{x_i\}\in\text{adiab.tr.}} = \frac{\partial V}{\partial\boldsymbol{u}(1)}\frac{\partial u^{(1)}}{\partial x_i} \propto u_i^{(1)}, \tag{2.13}$$

the effective mass can be expressed through the components of the eigenvector $\boldsymbol{u}^{(1)}$:

$$m(\text{stationary state}) = \sum_{i=1}^{N}\left(u_i^{(1)}\right)^2 \Bigg/ \left(\sum_{i=1}^{N}u_i^{(1)}\right)^2. \tag{2.14}$$

Using the definition (2.11), it is easy to show that

$$m \simeq \begin{cases} 1, & \text{if } g \to 0, \\ 1/N, & \text{if } g \to \infty. \end{cases} \tag{2.15}$$

Finally, using eq. (2.13) and the following relationships:

$$v_1^2 = \|\boldsymbol{v}^{(1)}\|^2 = \|\boldsymbol{u}^{(1)}\|^2 = \sum_{i=1}^{N}\left(u_i^{(1)}\right)^2,$$

$$(X - X_s)^2 = \left(\sum_{i=1}^{N}u_i^{(1)}\right)^2,$$

we obtain from expression (2.5) that near a stationary (minimum or saddle) state with a coordinate X_s, the potential energy of the system can be represented as

$$\epsilon(X) \simeq \text{const}(S) \pm \tfrac{1}{2}m\omega_s^2(X - X_s)^2, \tag{2.16}$$

where

$$\omega_s^2 = \pm\lambda_1 > 0. \tag{2.17}$$

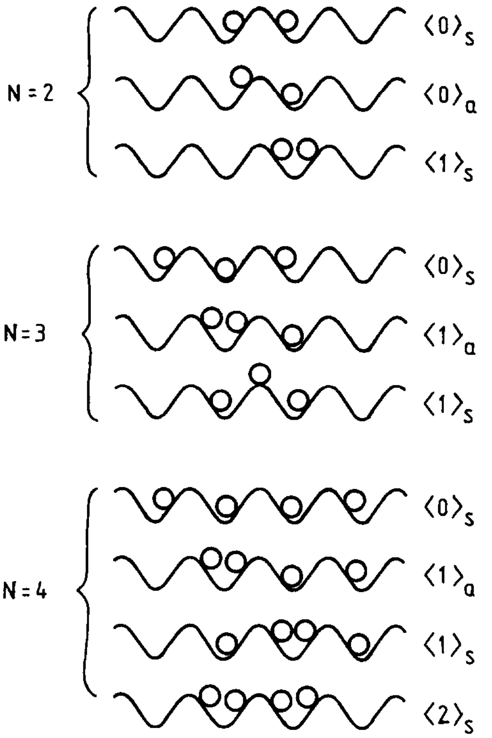

Fig. 1. Stationary-state configurations of the FK chain.

Let us number the minima of the external potential in a such manner that the first atom of the chain will occupy the potential well with the number 1, and the last (Nth) atom, the well with some number M. Then, it will be convenient to designate various stationary states of the system by the integer $n = N - M$, and also by an additional index "s" for symmetric and "a" for asymmetric states (see fig. 1). Moreover, to distinguish the states corresponding to the local minima of the potential energy from the saddle ones, we will highlight the former by underscoring ($\langle \underline{n} \rangle$), and the latter, by overscoring ($\langle \overline{n} \rangle$). Evidently, the state $\langle \underline{0} \rangle_{\mathrm{s}}$ will always be the ground one at $a = 2\pi$. As the parameter a decreases, the consequent change of the ground states, $\langle \underline{0} \rangle_{\mathrm{s}} \to \langle \underline{1} \rangle \to \langle \underline{2} \rangle \to \dots \to \langle \underline{n}^* \rangle$, takes place, where

$$n^* = \mathrm{int}[(N-1)/2]. \tag{2.18}$$

So, the problem is reduced to the calculation of characteristics of the adiabatic motion of the chain, $\epsilon(X)$, ϵ_{a}, m, and ω, from one ground state $\langle \underline{n} \rangle$ with the coordinate X_{i} to the neighbouring one with $X_{\mathrm{f}} = X_{\mathrm{i}} + b$.

3. Results of the calculations

In the two limiting cases, the determination of the characteristics of the system motion is trivial. Firstly, for noninteracting atoms ($g = 0$) we have $m = 1$, $\epsilon_{\mathrm{a}} = 2$, and $\omega = 1$. Secondly, for the strongly coupled atoms in the chain ($g = \infty$), the activation energy for chain's motion is determined by (1.5), the effective mass is equal to $m = 1/N$, and the frequency, eq. (2.17), is equal to

$$\omega = [\,|\sin(Na/2)|/N \sin(a/2)]^{1/2}. \tag{3.1}$$

Evidently, at $0 < g < \infty$ it is energetically favourable for chain atoms to be shifted away from the positions, eq. (1.2), to the nearest minima of the external potential. For short chains consisting of two and three atoms it is possible to obtain analytical results; they are given in appendices A and B. Here we describe the results of numerical investigation of the chain's motion for an arbitrary N, firstly for even N ($N = 4$ as an example), and then for odd N.

Let us recall that the ground state $\langle \underline{0} \rangle_{\mathrm{s}}$ should transfer to the states $\langle \underline{1} \rangle$, $\langle \underline{2} \rangle, \dots, \langle \underline{n}^* \rangle$ whenever the parameter a is reduced. Consequently, it is possible to define regions $\mathrm{O}_0, \mathrm{O}_1, \dots, \mathrm{O}_{n^*}$ on the parametric plane (a, g), so that in the region O_n the state $\langle \underline{n} \rangle$ is the ground one. For example, for $N = 4$ the region O_0 (with the ground state $\langle \underline{0} \rangle_{\mathrm{s}}$) includes regions a–c in fig. 2, and the region O_1 (with the ground state $\langle \underline{1} \rangle_{\mathrm{s}}$) includes regions d–i. The regions O_{n-1} and O_n are separated by the curve $[a_n]$ (see curve $[a_1]$ in fig. 2), where the value a_n is equal to that value of a which satisfies the equation $\epsilon(\langle \underline{n-1} \rangle) = \epsilon(\langle \underline{n} \rangle)$, so that the region O_n is determined by the inequality $a_{n+1} < a < a_n$.

Every region O_n is in turn divided by the curve $[\tilde{a}_n]$ (see curve $[\tilde{a}_1]$ in fig. 2) into two subregions, the "right" one, O_n^- ($\tilde{a}_n < a < a_n$), where the motion is carried out along the trajectory

$$\langle \underline{n} \rangle \to \langle n-1 \rangle \to \langle \underline{n} \rangle, \tag{3.2}$$

and the "left" subregion, O_n^+ ($a_{n+1} < a < \tilde{a}_n$),

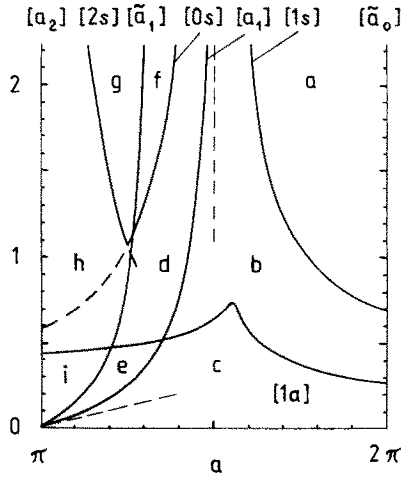

Fig. 2. Plane of system parameters (a, g) for the FK chain with $N = 4$. Definitions of curves see in text. The letters a–i designate the regions with different adiabatic trajectories: (a) $\langle \underline{0} \rangle_s \to \langle \bar{1} \rangle_s \to \langle \underline{0} \rangle_s$, (b) $\langle \underline{0} \rangle_s \to \langle \bar{x} \rangle \to \langle \underline{1} \rangle_s \to \langle \bar{x} \rangle \to \langle \underline{0} \rangle_s$, (c) $\langle \underline{0} \rangle_s \to \langle \bar{x}' \rangle \to \langle \underline{1} \rangle_a \to \langle \bar{x}'' \rangle \to \langle \underline{1} \rangle_s \to \langle \bar{x}'' \rangle \to \dots$, (d) $\langle \underline{1} \rangle_s \to \langle \bar{x} \rangle \to \langle \underline{0} \rangle_s \to \langle \bar{x} \rangle \to \langle \underline{1} \rangle_s$, (e) $\langle \underline{1} \rangle_s \to \langle \bar{x}' \rangle \to \langle \underline{1} \rangle_a \to \langle \bar{x}'' \rangle \to \langle \underline{0} \rangle_s \to \langle \bar{x}'' \rangle \to \dots$, (f) $\langle \underline{1} \rangle_s \to \langle \bar{0} \rangle_s \to \langle \underline{1} \rangle_s$, (g) $\langle \underline{1} \rangle_s \to \langle \bar{2} \rangle_s \to \langle \underline{1} \rangle_s$, (h) $\langle \underline{1} \rangle_s \to \langle \bar{x} \rangle \to \langle \underline{2} \rangle_s \to \langle \bar{x} \rangle \to \langle \underline{1} \rangle_s$, (i) $\langle \underline{1} \rangle_s \to \langle \bar{x}' \rangle \to \langle \underline{1} \rangle_a \to \langle \bar{x}'' \rangle \to \langle \underline{2} \rangle_s \to \langle \bar{x}'' \rangle \to \dots$.

where the adiabatic trajectory passes through the state $\langle n+1 \rangle$:

$$\langle \underline{n} \rangle \to \langle n+1 \rangle \to \langle \underline{n} \rangle. \tag{3.3}$$

For $N = 4$ the region O_1^- involves subregions d–f in fig. 2, and the region O_1^+ includes subregions g–i. According to the definition of the adiabatic trajectory, the curve $[\tilde{a}_n]$ is determined by a condition that the activation energies for the trajectories, eqs. (3.2) and (3.3) will equal to one another. Note that the straight line $a = 2\pi$ corresponds to the curve $[\tilde{a}_0]$, and the straight line $a = \pi$ coincides with the curve $[a_{n^*+1}]$ at even N, and with the curve $[\tilde{a}_{n^*}]$ at odd N.

In the region O_0 there is the curve [1s] (see fig. 2), to the right of which (i.e. at $a_{[1s]} < a < 2\pi$) the state $\langle 1 \rangle_s$ is the saddle one, and to the left of which the state $\langle 1 \rangle_s$ corresponds to the local minimum of the system energy. Similarly, in each region O_n^- (O_n^+) there exists the same curve $[(n-1)s]$ $(1[(n+1)s])$, to the left (right) from which the state $\langle \overline{n-1} \rangle_s$ $(\langle \overline{n+1} \rangle_s)$, and to the right (left) from which the state $\langle \underline{n-1} \rangle_s$ $(\langle \underline{n+1} \rangle_s)$ exist (see the curve [0s] in the region O_1^-, and the curve [2s] in the region O_1^+ in fig. 2).

Finally, in fig. 2 is plotted the curve [1a], below which the stationary state $\langle \underline{1} \rangle_a$ (see fig. 1) additionally appears, corresponding to the local minimum of the system energy (to be exact, the saddle state $\langle \bar{x} \rangle$ is splitted into three ones: $\langle \bar{x}' \rangle$, $\langle \underline{1} \rangle_a$, and $\langle \bar{x}'' \rangle$). Generally, there are curves $[na]$ ($n = 1, 2, \dots, \operatorname{int}[(N-1)/2]$) below which the stationary states $\langle \underline{n} \rangle_a$ exist; in the case of odd N, these curves are merged with the curves $[ns]$ at $a \to a_n^\infty$ (see appendix B). The additional difference of the case with odd N from that with even N consists in the presence of an asymmetric ground state in the case of odd numbers of N and $n \neq 0$ (see ref. [15]) (i.e. the ground state is additionally twice degenerated [13]; it is an analog of the Aubry transition [6] for an infinite chain). For example, for $N = 3$ the asymmetric state $\langle \underline{1} \rangle_a$ is

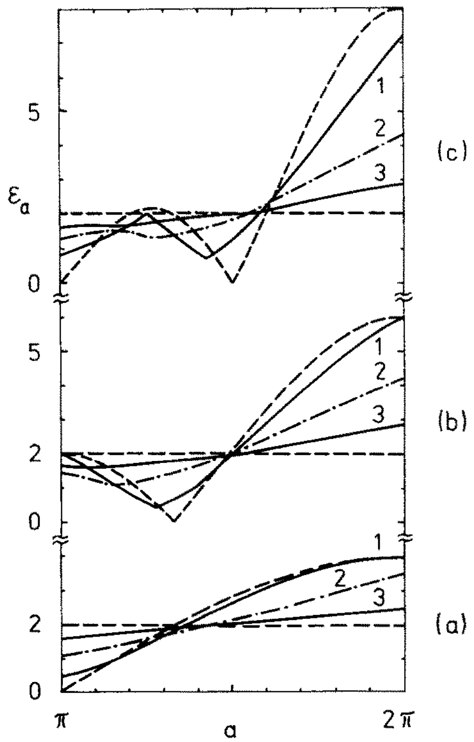

Fig. 3. Dependences of activation energy ϵ_a on parameter a for: (a) $N = 2$, (b) $N = 3$, and (c) $N = 4$. Broken curves correspond to values $g = \infty$ and $g = 0$, solid curves, to values $g = 1$ (curve 1) and $g = 0.1$ (curve 3), and chain curves, to values $g = 1/\pi$ for $N = 2$, and $g = 0.3$ for $N = 3$ and $N = 4$.

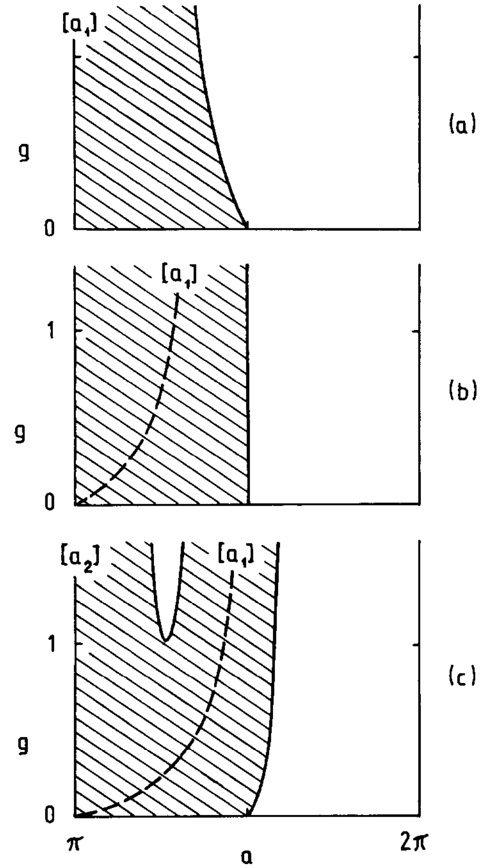

Fig. 4. Parametric plane (a, g) for: (a) $N = 2$, (b) $N = 3$, and (c) $N = 4$. Hatched areas show regions where activation energy for adiabatic motion of N-cluster is lower than for a single atom.

the ground one below the curve [1s] in the region O_1^- (see fig. 8 and the trajectories 5 and 6 in fig. 9 in appendix B).

Thus, the function $\epsilon_a(a)$ reaches its maximum at the commensurate case ($a = 2\pi$), has local maxima at $a = \tilde{a}_n$ and local minima at $a = a_n$ (see fig. 3). In vicinity of the curves $[a_n]$ there are regions on the parametric plane (a, g) (see hatched areas in fig. 4) where the activation energy for the motion of the chain is lower than that for the motion of an isolated atom.

4. Interpretation of the results

Let us now interpret the obtained results with the help of "solitonic" terminology. For an infinite atomic chain, commensurate with the external potential, there is a solution of motion's equation of the FK model, so-called kink, which describes the minimum possible topologically stable local compression of the chain. A kink is characterized by a half-width d,

$$d = 2\pi\sqrt{g}\,, \tag{4.1}$$

and an effective mass m,

$$m \simeq \begin{cases} 1, & \text{if } g \ll 1, \quad (4.2a) \\ 2/\pi^2\sqrt{g}\,, & \text{if } g \gg 1. \quad (4.2b) \end{cases}$$

The energy for the creation of a kink (with respect to the commensurate state of the chain with the same number of atoms) is equal to (see refs. [4,9])

$$\epsilon_k = \epsilon_k^{(0)} \mp 2\pi g(2\pi - a)\,, \tag{4.3}$$

where the upper (lower) sign corresponds to a kink (antikink), or chain's compression (expansion), and

$$\epsilon_k^{(0)} \simeq \begin{cases} 2\pi^2 g(1 - 2g)\,, & \text{if } g \ll 1, \quad (4.4a) \\ 8\sqrt{g}\,, & \text{if } g \gg 1. \quad (4.4b) \end{cases}$$

The motion of the kink is carried out in the periodic Peierls–Nabarro potential (see, e.g., refs. [9] and [10]) with the amplitude

$$\epsilon_p \simeq \begin{cases} 2 - \pi^2 g, \quad \text{if } g \ll 1, & (4.5a) \\ (16\pi^4/3)\, g \exp(-\pi^2\sqrt{g})\,, & \\ \quad \text{if } g \gg 1. & (4.5b) \end{cases}$$

Two kinks separated by a distance $x \gtrsim d$ repel one another with an energy (see refs. [9,17]).

$$\epsilon_{\text{rep}}(x) \simeq \begin{cases} 4\pi^2 g \exp(-\xi x/d)\,, & \\ \quad \text{if } g \ll 1, & (4.6a) \\ 32\sqrt{g}\, \exp(-x/d)\,, & \\ \quad \text{if } g \gg 1, & (4.6b) \end{cases}$$

where the numerical coefficient $\xi(g)(\xi < 1)$ was tabulated by Joos [9]. In the case of $g \gg 1$ (i.e. $d \gg 2\pi$) the motion equations of the FK model are reduced to the SG equation whose solution is the so-called knoadel wave, a periodic sequence of kinks of width kd, one period of the wave comprising L atoms,

$$L = g^{1/2} 2kK(k)\,, \tag{4.7}$$

and the modulus $k (0 < k \leqslant 1)$ being determined by the equation [8]

$$\frac{4}{\pi}(E(k)/k) = (2\pi - a)\sqrt{g}. \tag{4.8}$$

Here, $K(k)$ and $E(k)$ are the complete elliptic integrals of the first and second kinds, respectively.

For a semi-infinite atomic chain with a free end the solution of the SG equation is stable if the modulus k satisfies the following inequalities [4]:

$$(1 - k^2)^{1/2} \leqslant \tfrac{1}{2} k\sqrt{g}(2\pi - a) \leqslant 1. \tag{4.9}$$

For a finite atomic chain, the value of k is determined by the boundary condition for the second free end of chain [4], so that only a finite number of values $k = k_n$, $n_{\min} \leqslant n \leqslant n_{\max}$ are admitted [14].

Using "solitonic" terminology, the state $\langle n \rangle$ can be considered as the state with n kinks in the chain. In the commensurate case $(a = 2\pi)$, the state without kinks, $\langle 0 \rangle$, is the ground one. As the parameter a decreases, the energy of the state $\langle 0 \rangle$ increases and the energy of the state $\langle 1 \rangle$ decreases down to intersection of their plots at $a = a_1$ (see fig. 5), when the energy of creation of an additional kink, ϵ_k, becomes equal to zero. It follows from eqs. (4.3) and (4.4) that the curve $[a_1]$ is determined by the expression [4]

$$g_{[a_1]} \simeq \begin{cases} (a - \pi)/2\pi, & \text{if } g \ll 1, \quad (4.10\text{a}) \\ (4/\pi)^2/(2\pi - a)^2, & \text{if } g \gg 1. \quad (4.10\text{b}) \end{cases}$$

The state $\langle \underline{0} \rangle_s$ exists up to the values $g \leqslant g_{[0s]}$, the curve [0s] being determined by the inequality (4.9) at $k \to 1$,

$$g_{[0s]} \simeq 4/(2\pi - a)^2, \quad \text{if } g \gg 1. \tag{4.11}$$

At $a_2 < a < a_1$, the state with one kink is the ground state since the creation of a second kink is

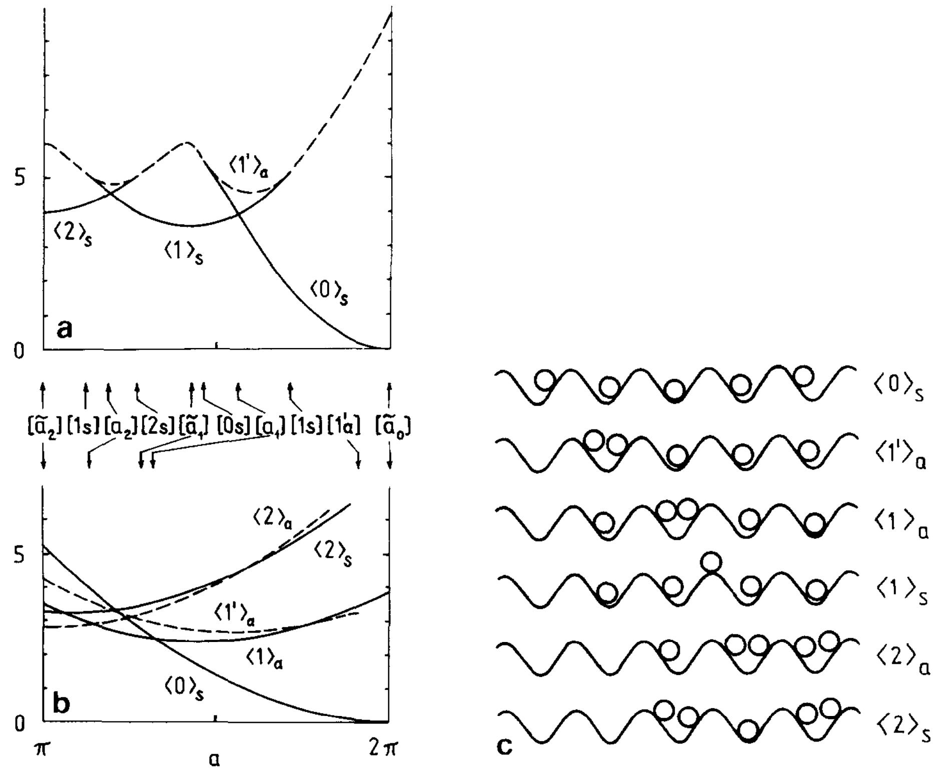

Fig. 5. Plot of energies of various states of the five-atomic FK chain versus equilibrium distance a at: (a) $g = 2$ and (b) $g = 0.3$; (c) stationary-state configurations of the chain with $N = 5$.

energetically unfavourable due to repulsion between the kinks (4.6). With further decrease of a, the energy $\epsilon(\langle 1\rangle)$ reaches its minimum and then rises (fig. 5). At the same time the energy $\epsilon(\langle 2\rangle)$ continues decreasing so that at $a = a_2$ the energies of the states $\langle \underline{1}\rangle$ and $\langle \underline{2}\rangle$ become equal to one another. Within the interval $a_3 < a < a_2$, the state with two kinks is the ground one, and so on up to the state $\langle n^*\rangle$. For small values of g, all the curves $[a_n]$ converge to the line determined by eq. (4.10a), because of an energy of kinks repulsion (4.6a) is exponentially small for small g. In the case of $g \gg 1$ (when $d \gg 2\pi$), the continuum approximation can be used to determine the curves $[a_n]$. If we neglect the boundary effects (i.e. if $N \gg 1$), then the energies of the states $\langle n-1\rangle$ and $\langle n\rangle$ for a finite chain become equal to one another, whenever the following condition is fulfilled:

$$nL = N. \tag{4.12}$$

It can be seen from eq. (4.8) that $k \to 0$ whenever $g \to \infty$ and $a \neq 2\pi$. Expanding the functions $K(k)$ and $E(k)$ into a series in small k, from eqs. (4.7), (4.8), and (4.12) after straightforward transformations we obtain the expression for the curve $[a_n]$:

$$g_{[a_n]} \simeq \frac{(n\pi/N)^{1/2}}{(2\pi - a)^2 (a_n^\infty - a)^{1/2}}. \tag{4.13}$$

Note that this expression is valid provided $(2\pi - a)\sqrt{g} \gg 1$.

It is evident that for a finite chain with a length l, $l \simeq a_s(N-2)$, the expressions (4.2b) – (4.6b), (4.10b), and (4.11) are valid as long as a kink can be "inserted" into the chain, i.e. whenever $g \ll g^*$, where the value of g^* is determined from the condition

$$2d = l, \tag{4.14}$$

so that $g^* \simeq (N/2 - 1)^2$. Otherwise, i.e. at $g \gg g^*$, all the chain's atoms move simultaneously, and the equation $\epsilon_k = 0$ is satisfied at $a = a_1^\infty$ (see equation (1.6)).

For the commensurate case ($a = 2\pi$), the adiabatic motion of a chain can be described in the following way (see refs. [12,14]: in the beginning, a kink is introduced from the left end of the chain, then it moves along the chain to the right and is annihilated at the right end. According to the work [11], the creation of a kink at the free end of a semiinfinite chain (with the coordinate $x = 0$) and its subsequent motion to the right can be qualitatively viewed as the creation of a kink-antikink pair at the point $x = 0$ of an infinite chain, and their subsequent motion in opposite directions (kink to the right, $x_k = x$, and antikink to the left, $x_a = -x$). Therefore, the energy of the system with one kink can be rewritten in the form:

$$\epsilon_k(x) \simeq \epsilon_k - \tfrac{1}{2}\epsilon_{rep}(2x) - \tfrac{1}{2}\epsilon_{rep}(4\pi N - 2x), \tag{4.15}$$

where the last two terms can be interpreted as an energy of attraction of the kink to the chain's free ends. Thus, the potential energy of the adiabatic chains' motion, $\epsilon(X)$, can be approximately presented by the expression

$$\epsilon(X) = \epsilon_k(X) + \epsilon_p(X), \tag{4.16}$$

where the second term describes the kink motion along the chain in the periodic Peierls–Nabarro potential, $\epsilon_p(X) \simeq \frac{1}{2}\epsilon_p(1 - \cos X)$. In case $g \to 0$ we have $\epsilon_p \to 2$ and $\epsilon_k \to 0$, and the function $\epsilon(X)$ has $(N-1)$ local minima. According to the equations (4.4) and (4.5), $\epsilon_p \to 0$ with an increase of g, and the energy ϵ_k is increased up to its saturation at $g \gtrsim g^*$. At the same time the local minima of the function $\epsilon(X)$ disappear; at first (at $g \lesssim 1$, when $2d \simeq 2\pi$) two minima which are the nearest to chain ends, then more remote from the ends and so on. Finally, when at $g \gtrsim g^*$ the kink cannot be "inserted" into the chain, the function ϵ(X) has only one maximum for the state $\langle \overline{1}\rangle_s$, and the "solitonic" terminology becomes unsuitable.

In the general case ($a \neq 2\pi$) with the ground state $\langle \underline{n}\rangle$ ($n \neq 0$), the adiabatic motion, eq. (3.3), can be viewed, according to refs. [12,14], as the creation of an additional kink at the left end of the chain, and then, after a number of displacements, the annihilation of the extreme right kink at the right end of chain (see fig. 6a). For the trajectory (3.2) with an intermediate state $\langle n-1\rangle$ the sequence of events is inverse: at first, the extreme right kink leaves the chain, and then a

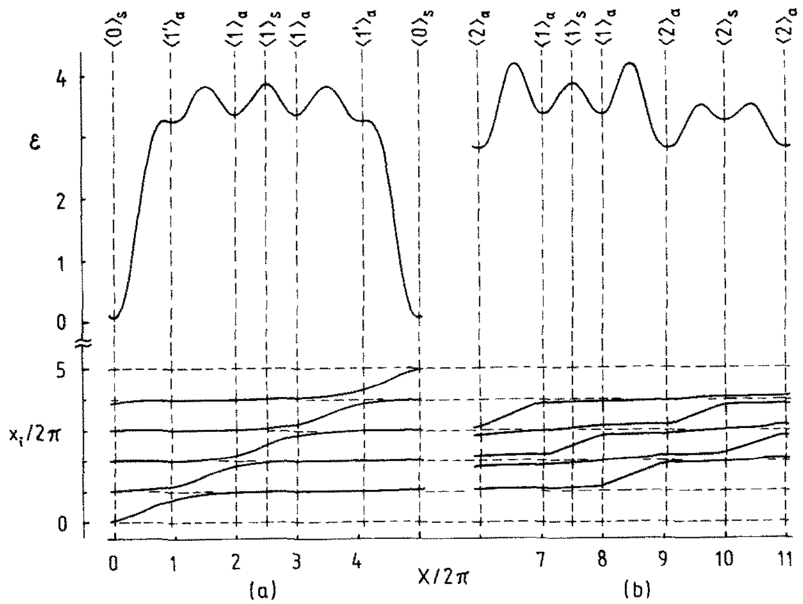

Fig. 6. Trajectories of adiabatic motion of the five-atomic FK chain for system parameters: $g = 0.3$ and (a) $a = 1.90\ \pi$, and (b) $a = 1.01\ \pi$.

new kink is created at the left end of the chain (see fig. 6b). Otherwise, the behaviour of the system at $a \neq 2\pi$ is qualitatively similar to that described above. So, the activation energy of the chain motion can be approximately represented as

$$\epsilon_a \simeq \Delta\epsilon_n(a,\ g) + \epsilon_p(g), \tag{4.17}$$

with

$$\Delta\epsilon_n = \min\{\ |\epsilon(\langle n+1\rangle) - \epsilon(\langle n\rangle)|,\ |\epsilon(\langle n-1\rangle) - \epsilon(\langle n\rangle)|\}. \tag{4.18}$$

Evidently, ϵ_a reaches minimum values whenever $\Delta\epsilon_n = 0$, i.e. at the curves $[a_n]$ of the plane (a, g). Therefore, near the curves $[a_n]$ there are regions, where the activation energy for the adiabatic motion of the N-atomic chain is lower than that for an isolated atom (see fig. 4). Note that at a fixed value of g for chains with various numbers of atoms, N, functions $\epsilon_a(a)$, $\omega(a)$, and $m(a)$ are weakly dependent on N as long as the inequality $2d \ll 1$ is satisfied (i.e. if $N \ll N^*$, where the value of N^* is determined by eq. (4.14). In particular, at $g \ll 1$ the dependence $\epsilon_a(a)$ has the form (A.10) (see Appendix A) for an arbitrary value of $N \geqslant 2$.

5. Discussion of the model

Now we discuss possible generalizations of the FK model. First of all, it is to be noted that the interaction between atoms should be described by more realistic potential than the harmonic one, e.g. by the Morse potential

$$v_{\text{int}}(x) = \epsilon_{\text{int}}\{\exp[-\gamma(x-a)] - 1\}^2, \tag{5.1}$$

where ϵ_{int} is the dissociation energy for two-atomic molecule, and $\gamma \simeq a^{-1}$ reflects the degree of anharmonicity of the interatomic potential. At small displacements away from the equilibrium state, $|x-a| \ll a$, we have

$$v_{\text{int}}(x) \simeq \tfrac{1}{2}g(x-a)^2[1-\gamma(x-a)],\ g = 2\epsilon_{\text{int}}\gamma^2. \tag{5.2}$$

Note that to estimate the value of g, it is convenient to return to dimensional units:

$$g = 2[\epsilon_{\mathrm{int}}/(\epsilon_{\mathrm{s}}/2)]\left[\gamma(a_{\mathrm{s}}/2)\right]^2. \tag{5.3}$$

As was shown by Markov and Milchev [18], the FK model with the Morse potential (5.1) has two novel features. Firstly, the symmetry between the kink (local contraction of the chain) and the antikink (local extension) is violated. As compared against the kink, the antikink is characterized by a lower value of ϵ_{k}, and by higher values of ϵ_{p} and m, the difference in kink–antikink parameters being proportional to γ. As a result, the curves $[a_n]$ and $[\tilde{a}_n]$ on the plane (a, g) will be shifted. For example, at $a = 2\pi$ the trajectory $\langle 0\rangle \to \langle -1\rangle \to \langle 0\rangle$ will have the lower activation energy than the trajectory $\langle 0\rangle \to \langle +1\rangle \to \langle 0\rangle$. Secondly, for the potential (5.1) the interatomic attraction force is reduced with an increase of distance between atoms. As a result, an infinite number of metastable states of the system appears, which correspond to the chain rupturing into two, three, N parts (or single atoms). So, at some parameters of the system there may be an adiabatic trajectory corresponding to chain's rupture (i.e. its dissociation).

Above we have considered only the adiabatic (i.e. infinitely slow) motion of a chain. If the chain moves at some finite velocity $\dot{X}$, the "dynamic" Peierls potential will differ from the adiabatic one. Indeed, at velocities $\dot{X} \gtrsim b\omega$ the atoms of the chain will have no time to adjust to the external (substrate) potential; this is equivalent to effective decrease of the external potential amplitude. Besides, as was shown by Kovalev [11], in the case of $a \simeq \tilde{a}_n$ due to inertia of the chain, its motion should be carried out along the trajectory

$$\langle n\rangle \to \langle n+1\rangle \to \langle n\rangle \to \langle n-1\rangle \to \langle n\rangle \to \dots, \tag{5.4}$$

because the kink is transformed into the antikink during its reflection from a free end of the chain. This motion, reminiscent of a crawling caterpillar, has a more "straight" trajectory in a phase space.

6. Diffusion of adsorbed clusters

To describe a behaviour of real systems, an energy exchange between various degrees of freedom of the FK chain as well as between the chain and the substrate should be taken into account. Phenomenologically, this exchange leads to a friction with some coefficient η which is proportional to the rate of energy exchange (e.g., ref. [19]). Thus, the motion of the chain can be approximately described by the Langevin equation

$$m\ddot{X} + m\eta\dot{X} + \partial\epsilon(X)/\partial X = \delta F, \tag{6.1}$$

where the stochastic force δF satisfies the fluctuation–dissipation theorem, $\langle \delta F(X, t)\, \delta F(X, t')\rangle = 2\eta(X) m(X) k_{\mathrm{B}} T\, \delta(t - t')$, and T is the temperature of the system. Of course, thermal fluctuations of positions and velocities of chain and substrate atoms modify the function $\epsilon(X)$ in equation (6.1). The corresponding errors can be lowered if the value of ϵ_{s} is taken as the experimentally measured value of the activation energy of diffusion of a single atom.

It is well known that for times $t > \eta^{-1}$, a solution of the Langevin equation (6.1) describes a diffusion motion of the system with a diffusion coefficient

$$D = Rb^2, \quad R = R_0 \exp(-\epsilon_{\mathrm{a}}/k_{\mathrm{B}}T), \tag{6.2}$$

where R is the rate of escape of the system from the bottom of the potential well of $\epsilon(X)$. Neglecting a complicated form of the function $\epsilon(X)$ (namely, ignoring the local minima existence), the energy $\epsilon(X)$ can be approximated by the function, initially introduced by Peyrard and Remoissenet [20]:

$$\epsilon(X) \simeq \tfrac{1}{2}\epsilon_{\mathrm{a}} v_{\mathrm{p}}(2\pi X/b),$$
$$v_{\mathrm{p}}(y) = \frac{(1-r)^2(1-\cos y)}{(1 + r^2 + 2r\cos y)}, \tag{6.3}$$

where r is some parameter ($|r| < 1$). Then the eigenfrequencies ω_0 (at the minimum of the potential $\epsilon(X)$) and ω_{s} (at the saddle point), $\omega_{0,\mathrm{s}}^2 = m_{0,\mathrm{s}}^{-1}\epsilon''(\mathrm{X})\,|_{X=0;\ b/2}$, can be connected by the following relationship:

$$m_0\omega_0^2 m_{\mathrm{s}}\omega_{\mathrm{s}}^2 = \left(\epsilon_{\mathrm{a}}/2N^2\right)^2. \tag{6.4}$$

Excluding an exotic case of extremely low friction (see, e.g., ref. [19]), a pre-exponential factor R_0 for the potential (6.3), (6.4) is determined by the Kramers theory [21]:

$$R_0 \simeq \begin{cases} \omega_0/2\pi, & \text{if } \eta \lesssim \omega_s, \quad (6.5a) \\ \omega_0\omega_s/2\pi\eta, & \text{if } \eta > \omega_s. \quad (6.5b) \end{cases}$$

Using eqs. (6.2), (6.4), and (6.5), we obtain the expression for the diffusion coefficient:

$$D = D_0 \exp(-\epsilon_a/k_B T), \tag{6.6}$$

$$D_0 \simeq \begin{cases} 2\pi N^2\omega_0, & \text{if } \eta \lesssim \omega_s, \quad (6.7a) \\ \pi\epsilon_a/\eta\sqrt{m_0 m_s}, & \text{if } \eta > \omega_s. \quad (6.7b) \end{cases}$$

If the potential (6.3) has a shape of deep narrow wells separated by wide barriers (i.e. if $r < 0$), we can approximately take $\epsilon_a \simeq \frac{1}{2} m_0 \omega_0^2 \pi^2$, so that the following estimation for the value of D_0 is obtained:

$$D_0 \simeq \begin{cases} 2\pi N^2\omega_0, & \text{if } N \leqslant N^{**}, \quad (6.8a) \\ 2\pi\omega_0^2/\eta, & \text{if } N > N^{**}, \quad (6.8b) \end{cases}$$

where

$$N^{**} = (\omega_0/\eta)^{1/2}. \tag{6.9}$$

Thus, for the commensurate case ($a = 2\pi$) at a fixed value of g, both the activation energy ϵ_a (up to the saturation at $N \gtrsim N^*$, where N^* is determined by eq. (4.14)) and the pre-exponential factor D_0 (up to the saturation at $N \gtrsim N^{**}$) increase with the increase of the chain's length, N. On the other hand, at fixed values of N and g the factors ϵ_a, ω_0, and D_0 change "in-phase" (usually decrease, see fig. 3)), when reducing the equilibrium distance a. So in both cases the theory predicts the existence of a "compensation" effect, i.e. the values ϵ_a and D_0 are changed simultaneously in the same direction. Note that this effect is observed in a number of experiments (see, e.g., ref. [3]). The diffusion coefficient D can both increase and decrease with the increase in a chain length, N, the former situation taking place at $a \simeq \tilde{a}_n$, and the latter, at $a \simeq a_n$.

The FK model is naturally used to describe static and dynamic properties of layers adsorbed on metal or semiconductor surfaces (see e.g. ref. [22]). Surface diffusion of adatoms or admolecules is extensively investigated by various experimental techniques (see ref. [3]), including computerized simulation (see refs. [23,24]). To estimate the parameter g for adsystems, let us take $\epsilon_s \simeq 0.1$ eV for the activation energy of diffusion of a single adatom [3], $\epsilon_{int} \simeq 0.05$–$0.5$ eV for the interaction energy between two neighbouring adatoms (see survey [25]), and put $\gamma a_s \simeq 1$ into eq. (5.3). As a results, we obtain $g \simeq = 0.05$–0.5, which corresponds to the case of a weak bond. However, when atoms of small radii ($a < a_s$) are adsorbed, then $\gamma \simeq (a_s/a) > 1$, and the case of intermediate coupling, $g \gtrsim 1$, can be carried out. In the case of adsystems, the energy exchange between adatoms and substrate atoms usually leads to a friction coefficient $\eta \simeq (0.01 - 1)\omega_0$ (see ref. [19]) and, as the estimates show, this friction mechanism is the main one. Thus, we obtain the estimation $N^* \approx N^{**} \approx 1$–$10$. However, it should be noted that for adsystems the parameters ϵ_{int}, γ, and η are not constant because they depend on the electronic structure of the substrate, its temperature, and the concentration of adatoms [19,25].

Observation of the motion of single adatoms and their clusters with the use of field ion microscope have shown that on the smoothed crystal faces (for example, on the face (110) of tungsten) the mobility of clusters is reduced with an increase of the number of atoms forming the cluster [26]. Similar behaviour was observed on the "furrowed" crystal faces (i.e. on the face (112) of tungsten) for the motion of a linear cluster which is completely disposed inside one furrow [26–29]. However, if different atoms of the cluster are placed into different (neighbouring) furrows of the furrowed crystal face, then the mobility of the cluster is sufficiently high, i.e. is close to the mobility of a single adatom [26–29]. Such behaviour can be explained in the following way: the case of smoothed faces is close to the commensurate case of $a \simeq a_s$, while in the case of atomic adsorption in the neighbouring furrows on the furrowed faces the situation may arise with $0 < a < a_s$.

When a parameter of the adsystem, e.g. temperature T or adatomic concentration θ is changed, various phase transitions can occur in the adlayer [22]. For the phase transition of the first kind, it was experimentally observed that when the system is approaching the phase transition point, the diffusion coefficient D increases in some cases (e.g., for adsystems Ba–Mo(110) [30] and Li–Mo(110) [31]) as well as it decreases in other cases (e.g., for Li–W(110) [32], Ba–W(110) [33], and La–W(110) [34]). Such behaviour of D can be explained by the creation of two-dimensional islands (clusters) of a new phase against the background of the old phase due to fluctuations of the adatomic concentration in the fluctuation region of the first-kind phase transition. Depending on the parameters of an adsystem, the mobility of these islands may either exceed the mobility of adatoms in the old phase, or may be lower than the latter.

7. Concluding remarks

We have investigated the adiabatic motion of a one-dimensional cluster formed by atoms attracting one another and placed into the external periodic potential. The results have demonstrated that the mobility of clusters can either decrease (for the commensurate case of $a \simeq j a_s$, j being an integer) or increase (at $a \simeq (j+\frac{1}{2})a_s$) with the increase of a cluster size. It should be reminded that for an infinite chain of atoms, the dynamics of the FK model does not depend on the parameter a (see ref. [9]).

In the present paper, the main point of our interest has been how can the FK model explain some experimental data on surface diffusion of adatoms. It should be noted that the FK model can also be applied to a number of other physical systems which have been briefly mentioned in the section 1, so the results may be applied to that systems.

Acknowledgements

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Appendix A: case of $N = 2$

The two-atomic cluster has three stationary states: $\langle 0\rangle_s$, $\langle 0\rangle_a$, and $\langle 1\rangle_s$ (see fig. 1). The state $\langle 0\rangle_s$ is always the ground one, and it has atomic positions $x_1 = z_0$, $x_2 = 2\pi - z_0$, where the value of z_0 $(0 \leqslant z_0 \leqslant \pi/2)$ is determined by a solution of the transcendental equation

$$\sin z_0 = 2g\left[(\pi - a/2) - z_0\right]. \tag{A.1}$$

In limiting cases, this equation has approximate solutions:

$$z_0 \simeq \begin{cases} (2\pi - a)g/(1+2g), & \text{at } g \ll 1, \\ (\pi - a/2) - \left[\sin(\pi - a/2)\right]/2g, & \\ \quad \text{at } g \gg 1. \end{cases} \tag{A.2}$$

It can be easily shown that the state $\langle 0\rangle_s$ is characterized by the following parameters: $m(\langle 0\rangle_s) = 1/2$,

$$\begin{aligned} \epsilon(\langle 0\rangle_s) &= 2\left[1 - \cos z_0 + g(\pi - a/2 - z_0)^2\right] \\ &\simeq \begin{cases} \frac{1}{2}g(1-2g)(2\pi - a)^2, & \text{at } g \ll 1, \\ 2[1 - \sin((a-\pi)/2)] & \\ \quad -(1/2g)\sin^2(a/2), & \text{at } g \gg 1, \end{cases} \end{aligned} \tag{A.3}$$

and

$$\begin{aligned} \omega^2(\langle 0\rangle_s) &= \cos z_0 \\ &\simeq \begin{cases} 1 - \frac{1}{2}g^2(2\pi - a)^2, & \text{at } g \ll 1, \\ \sin((a-\pi)/2) + (1/2g)\sin^2(a/2), & \\ \quad \text{at } g \gg 1. \end{cases} \end{aligned} \tag{A.4}$$

The state $\langle 1\rangle_s$ with atomic positions $x_{1,2} = \pm z_0'$ (see fig. 1), where the value of z_0' $(0 \leqslant z_0' \leqslant \pi)$ is determined by the equation

$$\sin z_0' = 2g(a/2 - z_0'), \tag{A.5}$$

is characterized by the effective mass $m(\langle 1\rangle_s) =$

1/2, the energy

$$\epsilon(\langle 1\rangle_s) = 2\left[1-\cos z_0' + g(z_0'-a/2)^2\right]$$
$$\simeq \begin{cases} \frac{1}{2}g(1-2g)a^2, & \text{at } g \ll 1, \\ 2\left[1+\sin((a-\pi)/2)\right] \\ \quad -(1/2g)\sin^2(a/2), & \text{at } g \gg 1, \end{cases} \tag{A.6}$$

and by the minimum eigenvalue

$$\lambda_1 = \cos z_0'. \tag{A.7}$$

According to (A.7), the value $\lambda_1 > 0$ whenever $z_0' < \pi/2$, and $\lambda_1 < 0$ whenever $z_0' > \pi/2$. Substituting the critical value $z_0' = \pi/2$ into equation (A.5), we obtain an equation of the curve [1s],

$$g_{[1s]} = (a-\pi)^{-1}, \tag{A.8}$$

which divides the plane (a, g) of the system parameters into two parts: the "upper" one, $g > g_{[1s]}$ (or the "right-hand" one, $a > a_{[1s]}$), where the state $\langle 1\rangle_s$ is the saddle state, and the "lower" part, $g < g_{[1s]}$ (or the "left-hand" one, $a < a_{[1s]}$), where the state $\langle 1\rangle_s$ corresponds to the local minimum of the potential energy of the system.

In the "lower" part of parametric plane there also exists the stationary state $\langle 0\rangle_a$ (see fig. 1) with atomic positions $x_2 = \pi + x_1$, $x_1 = -\sin^{-1}[g(a-\pi)]$. This state corresponds to the saddle point of the trajectory, and is characterized by the energy

$$\epsilon(\langle 0\rangle_a) = 2 + \tfrac{1}{2}g(a-\pi)^2. \tag{A.9}$$

Thus, if the system parameters belong to the "upper" part, the dimer moves along the trajectory $\langle \underline{0}\rangle_s \to \langle \bar{1}\rangle_s \to \langle \underline{0}\rangle_s$ (see trajectory 1 in fig. 7) with the activation energy $\epsilon_a = \epsilon(\langle \bar{1}\rangle_s) - \epsilon(\langle \underline{0}\rangle_s)$, and in the "lower" part of the parametric plane the motion is carried out along the trajectory $\langle \underline{0}\rangle_s \to \langle \bar{0}\rangle_a \to \langle \underline{1}\rangle_s \to \langle \bar{0}\rangle_a \to \langle \underline{0}\rangle_s$ (see trajectories 2 and 3 in fig. 7) with an activation energy $\epsilon_a = \epsilon(\langle \bar{0}\rangle_a) - \epsilon(\langle \underline{0}\rangle_s)$. The function $\epsilon_a(a)$ at different values of g is plotted in fig. 3a, and the corresponding trajectories of the adiabatic motion of the dimer, $x_1(X)$ and $x_2(X)$, as well as the potential energy $\epsilon(X)$ are shown in fig. 7. In the case of weak coupling between atoms the following expression for the activation energy can be derived from eqs. (A.3) and (A.9):

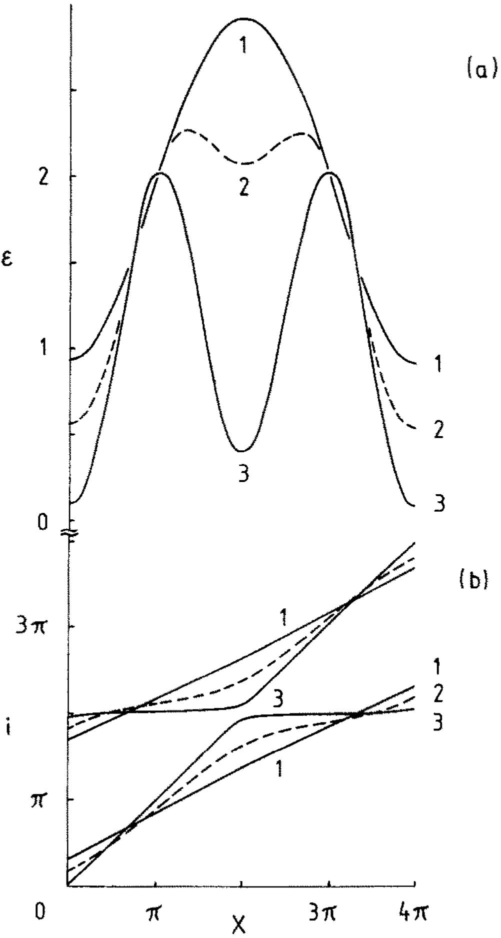

Fig. 7. Plot of dependences of (a) potential energy ϵ and (b) atomic coordinates x_1 and x_2 on coordinate X for adiabatic motion of dimer. System parameters: $a = 4\pi/3$ and $g = 5$ (curve 1), 0.5 (curve 2, dashed), and 0.05 (curve 3).

$$\epsilon_a \simeq 2 + \pi g(a - 3\pi/2), \quad g \ll 1. \tag{A.10}$$

From eqs. (1.5) and (A.10) it is seen that the activation energy of motion of the dimer is lower than for motion of a single atom as long as $(a-\pi) < \pi/3$ at $g \gg 1$, and if $(a-\pi) < \pi/2$ at $g \gg 1$ (see hatched area in fig. 4a).

Appendix B: case of $N = 3$

In the case of $N = 3$, only the symmetric states $\langle 0\rangle_s$ and $\langle 1\rangle_s$ (see fig. 1) can be analytically considered. For the state $\langle 0\rangle_s$ with atomic positions $x_1 = z_0$, $x_2 = 2\pi$, and $x_3 = 4\pi - z_0$, where z_0 is determined by the equation

$$\sin z_0 = g[(2\pi - a) - z_0], \tag{B.1}$$

the potential energy is equal to

$$\epsilon(\langle 0\rangle_s) = 2(1 - \cos z_0) + g(2\pi - a - z_0)^2. \tag{B.2}$$

The lowest root of the quadratic equation,

$$\lambda^2 - \lambda(\cos z_0 + 3g + 1) + (1 + 2g)\cos z_0 + g = 0, \tag{B.3}$$

is associated with the eigenvalue λ_1. It can be seen that λ_1 turns to zero whenever

$$\cos z_0 = -g/(1 + 2g). \tag{B.4}$$

From eqs. (B.1) and (B.4) we obtain that the curve [0s] is determined by the equations

$$\begin{cases} 2\pi - a = z_0 + g^{-1}\sin z_0, \\ z_0 = \cos^{-1}[-g/(1 + 2g)], \end{cases} \tag{B.5}$$

so that at $g \to \infty$ this curve takes the form

$$g_{[0s]} \simeq 1/(4\pi/3 - a)\sqrt{3}, \quad \text{if } a \to 4\pi/3 - 0. \tag{B.6}$$

Above ($g > g_{[0s]}$), or to the left ($a < a_{[0s]}$) from the curve [0s], the state $\langle 0\rangle_s$ is the saddle one, and below (or to the right) this state corresponds to the local minimum of the energy.

Similarly, for the state $\langle 1\rangle_s$ with atomic positions $x_1 = -z_0'$, $x_2 = \pi$, and $x_3 = 2\pi + z_0'$, where z_0' is determined by the equation

$$\sin z_0' = g[(a - \pi) - z_0'], \tag{B.7}$$

the curve [1s] is determined by the equations

$$\begin{cases} a - \pi = z_0' + g^{-1}\sin z_0', \\ z_0' = \cos^{-1}[g/(2g - 1)]. \end{cases} \tag{B.8}$$

It is evident that $g_{[1s]} \geqslant 1$. At $g \to \infty$, from (B.8) we obtain:

$$g_{[1s]} \simeq 1/(a - 4\pi/3)\sqrt{3} \text{ if } a \to 4\pi/3 + 0. \tag{B.9}$$

As distinct from the case of even N, in the present case the shape of the curve [1s] is more complicated (compare figs. 2 and 8): it is bent to the left with the decrease of g, so that at $g \gtrsim 1$

$$g_{[1s]} \simeq 1 + (1/8)(a - \pi)^2, \quad \text{if } a \to \pi + 0. \tag{B.10}$$

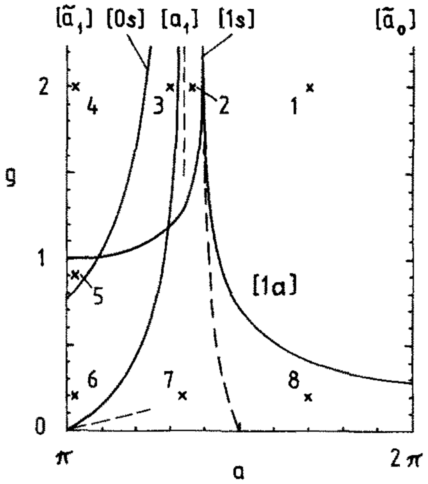

Fig. 8. Parametric plane (a, g) for three-atomic chain. Crosses with numbers 1 to 8 designate system parameters used to calculate adiabatic trajectories shown in fig. 9.

To the right ($a > a_{[1s]}$) from the curve [1s] the state $\langle 1\rangle_s$ is the saddle one, and to the left it corresponds to the energy local minimum.

The parametric plane (a, g) for the three-atomic chain is shown in fig. 8. There are two regions, O_0^+ and O_1^- (separated by the curve $[a_1]$) characterized by different mechanisms of the chain's motion. The curve [1s] divides the region O_1^- into two subregions: the "upper" one, O_{1s},

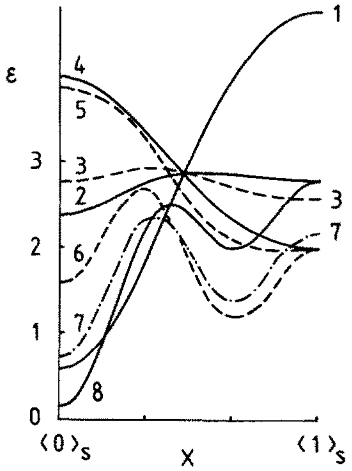

Fig. 9. Potential energy $\epsilon(X)$ of three-atomic chain during its adiabatic motion for different system parameters (see crosses in fig. 8): $(a, g) = (1.70\pi, 2)$; $(1.36\pi, 2)$; $(1.30\pi, 2)$; $(1.02\pi, 2)$; $(1.02\pi, 0.9)$; $(1.02\pi, 0.2)$; $(4\pi/3, 0.2)$; $(1.70\pi, 0.2)$.

where the state $\langle 1 \rangle_s$ is the ground one, and the "lower" subregion, O_{1a}, where the state $\langle 1 \rangle_a$ is the ground state. Another difference from the case of even N consists in the fact that the curve [1a], separating the subregion where the state $\langle 1 \rangle_a$ exists, is merged with the curve [1s] whenever a is reduced ($a \to 4\pi/3$). So, there are seven different types of adiabatic trajectories which are plotted in fig. 9. The dependent $\epsilon_a(a)$ for different values of g is shown in fig. 3b.

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