

Self-organization of stressed surfaces: The role of local relaxations

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(Received 21 July 1999)

We investigate, in a very simple form and using a continuum approach, the influence of the Frenkel-Kontorova mechanism on the self-organization of stressed chemisorbed layers on an anisotropic surface. The long-range substrate-mediated interactions are still the driving force for self-organization but short-range relaxations of the adsorbate domains play an important role. When the adsorbate film includes dislocations at high coverage, special values of the adsorbate domain size are favored. Surprisingly, short-range relaxations are still important for registered adsorbate films leading to modifications of Marchenko predictions.

The importance of the effects of surface stress on the morphology of surfaces is now well recognized.¹ Using the elastic theory of continuous media, Marchenko² has shown that the difference in stress between two bidimensional phases produces long-range interactions, which lead to periodic domain patterns: the period selected by the Marchenko mechanism is due to a balance between the domain boundary energy and the long-range elastic interactions.^{2,3} In this approach, as pointed out by Alerhand *et al.*,³ local relaxations are supposed to play a small role: they only contribute to the precise value of the domain boundary energy which is taken independent on the domain size. However, local relaxations are all the more important in surface science leading to various features: reconstruction, superstructures, commensurate-incommensurate transitions, dislocations networks, etc. One standard approach to tackle this problem is the Frenkel-Kontorova model,⁴ which treats the equilibrium of a harmonic chain standing on a sinusoidal potential. Frank and van der Merwe⁵ have indicated how to study the dependence of the Frenkel-Kontorova chain energy on its size. This dependence is not linear as assumed in the Marchenko approach. The purpose of this paper is to investigate the influence of the local relaxations of an adsorbate phase in the selection of a period by the Marchenko mechanism. Considering the adsorbate phase as a Frenkel-Kontorova chain, we will try to answer two main questions. Does a geometrical misfit between the adsorbate layer and the substrate favor the selection of special domain sizes? What is the role of edge relaxations for a dislocation-free chain?

The Marchenko approach considers the elastic response of the substrate to the difference in surface stresses, σ_A , σ_B , between two surface phases *A* and *B*. This difference in stress is equivalent to forces concentrated on the *A/B* boundaries and proportional to $(\sigma_A - \sigma_B)$. For a surface presenting alternating stripes of *A* and *B* of widths l_A and l_B and of period $L = l_A + l_B$, the elastic energy per unit area due to substrate-mediated elastic interactions has been shown to be^{2,3}

$$\Delta E = -\frac{C_2}{L} \ln \left[\frac{L}{2\pi a} \sin(\pi\tau) \right], \quad (1)$$

where a is a microscopic cutoff length, $\tau = l_A/L$ is the coverage and C_2 is given by

$$C_2 = \frac{1-\nu}{\pi g} (\sigma_A - \sigma_B)^2, \quad (2)$$

g and ν being the shear modulus and the Poisson ratio of the substrate. The total energy per unit area is

$$U_M(L) = \frac{C_1}{L} - \frac{C_2}{L} \ln \left[\frac{L}{2\pi a} \sin(\pi\tau) \right], \quad (3)$$

C_1 being the energy per unit length of the *A/B* domain boundaries. It includes the effects of dangling bonds and local relaxations. The minimization of U_M leads to

$$L = \frac{\kappa}{\sin(\pi\tau)}, \quad l_A(\tau) = l_B(1-\tau) = \frac{\kappa\tau}{\sin(\pi\tau)}, \quad (4)$$

with

$$\kappa = a2\pi \exp \left(1 + \frac{C_1}{C_2} \right). \quad (5)$$

Several comments must be made.

Since, in this continuum approach, small scale relaxations are neglected, the microscopic cutoff, a , remains undefined. Here, we will consider them explicitly and we take a to be the interatomic distance in the whole paper. Thus C_1 contains mainly ‘‘dangling-bond’’ effects.

Neither C_1 nor C_2 are precisely known. Because of the exponential dependence of κ on C_1/C_2 , this ratio must be of order one when κ is not macroscopic ($\kappa/a = 4 \times 10^5$ for $C_1/C_2 = 10$). This exponential dependence leads to a high sensitivity of L to C_1 variations.

In the Marchenko energy, both the phases participate only by their boundaries, therefore they play symmetric roles with respect to the transformation $\tau \rightarrow 1 - \tau$. Consequently, the width l_A at low coverage and the width l_B at high coverage have the same value κ/π .

Nevertheless, when one of the two phases is an adsorbed phase, its local organization may play a role in relaxations leading to an asymmetric role in the energy. The Frenkel-Kontorova model allows us to examine this local organization since its purpose is to study the equilibrium configuration of a harmonic chain submitted to a periodic sinusoidal potential (see Fig. 1).

The energy is written

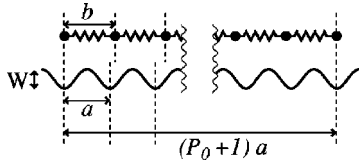


FIG. 1. The Frenkel-Kontorova model.

$$H_{FK} = \frac{1}{2} \mu \sum_{n=0}^{N-1} (x_{n+1} - x_n - b)^2 + \frac{1}{2} W \sum_{n=0}^{N-1} \left(1 - \cos \frac{2\pi x_n}{a} \right), \quad (6)$$

where μ is the force constant of the springs between atoms of the chain, b is their length at rest, a is the wavelength of the periodic potential, $W/2$ its amplitude, and x_n is the coordinate of the n th atom of the chain. The standard treatment of this problem in the continuum approximation has been performed by Frank and van der Merwe.⁵ They found, that for the infinite chain, the position of the n th atom is given by the solution of

$$\frac{d\xi}{dn} = \pm \left(\frac{1}{l_0 k} \right) (1 - k^2 \cos^2 \pi \xi)^{1/2}, \quad (7)$$

where $\xi = x/a - n$, $l_0 = (\mu a^2 / 2W)^{1/2}$, and $0 \leq k \leq 1$ is an integration constant. The chain consists of regions where ξ is nearly constant and integer, i.e., where the atoms are in or close to troughs of the substrate potential, separated by misfit dislocations. The typical width of a dislocation is l_0 . Studying a chain of l atoms with free edges (l is the chain length in a units and we call it *length* in the whole paper), Frank and van der Merwe noted that the solution may be obtained by cutting the infinite chain at the points of null spring tension. Their positions, $m \pm \xi_0$, depend on k and on $P_0 = a/(b - a)$, the coincidence mesh. The chain starting at $\xi = 1 - \xi_0$ and ending at $\xi = 1 + m + \xi_0$ contains m dislocations. Its length l is given by integration of Eq. (7) and its energy by integration of Eq. (6).

Thus, one obtains for each value of m a curve $E_m(l)$ parametrized by k (Fig. 2).⁶ Depending on the ratio l_0/P_0 , the different branches may or may not intersect. For $l_0/P_0 > 2/\pi$, the branches intersect and the number of dislocations in the stable chain increase with its length. For $l_0/P_0 < 2/\pi$ the chain without dislocations is always stable.

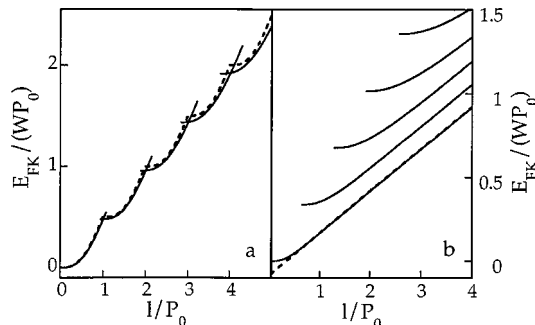


FIG. 2. Energy chain versus length for chains with zero, one, two, three, and four dislocations. (a) $l_0/P_0 = 2$, the dashed line is the approximant, (b) $l_0/P_0 = 0.5$, the dashed line is the asymptote.

Let us first study the state with dislocations. The change of branch in the stable solution corresponds to the nucleation of one dislocation and occurs when the length l approaches a multiple of the coincidence mesh. As seen in Fig. 2(a), for $l_0/P_0 > 2$ the energy is well approximated by

$$E_{FK}(l) \sim \frac{WP_0}{2} \left(\frac{l}{P_0} - \frac{|\sin(\pi l/P_0)|}{\pi} \right). \quad (8)$$

This asymptotic result is easily obtained by considering the infinitely rigid chain. In this limiting case, all the springs are at rest and the energy is simply obtained by integration of the substrate potential. The absolute value of the sine is due to the change of the position of the central atom: when the edge atoms are on the top of the substrate potential, a translation of the whole chain by half a period has zero energy cost, while allowing a better configuration for further growth: two half dislocations on the edges are replaced by a central one. While the critical value for the ratio l_0/P_0 is $2/\pi$, the asymptotic range is reached already for $l_0/P_0 > 2$, therefore the asymptotic expression of $E_{FK}(l)$ may be used as the generic approximant for the energy in the state with dislocations. The multiples of the coincidence mesh correspond to maxima of $E_{FK}(l)/l$ and *not* to minima as frequently stated.

Let us now study the state without dislocations. The asymptotic behavior of the energy for large l is given by

$$E_{FK}(l) \sim W \left(\frac{l_0}{P_0} \right)^2 \left(l - \frac{2l_0}{\pi} \right) = \frac{\mu(b-a)^2}{2} \left(l - \frac{2l_0}{\pi} \right). \quad (9)$$

The slope with respect to l is trivial: in the chain without dislocations, the springs are elongated by $(b - a)$. The precise value $2l_0/\pi$ of the intersection of the asymptote with the l axis is model dependent but its proportionality to l_0 is easily understandable: the relaxations at the chain edges, quite similar to a half dislocation, extend over a range l_0 , consequently these edge relaxations no longer interact when $l \gg l_0$.

In order to blend the Frenkel-Kontorova approach with the Marchenko one, we must examine the compatibility of their basic assumptions.

When writing Eq. (6), the deformation of the substrate is neglected since the substrate potential is unaffected by adsorbate relaxations. *A priori*, this may seem incompatible with the Marchenko approach where the basic ingredient is the elastic energy of the substrate. Nevertheless a substrate with high Lamé coefficients (stiff substrate) will have a noticeable elastic energy leading to a Marchenko mechanism together with a small strain as needed for a Frenkel-Kontorova description of the chain structure.

Due to the action-reaction principle, the Frenkel-Kontorova chain exerts a nonuniform stress on the substrate via the potential W . This stress depends on the chain length.⁶ A full calculation of the elastic response of the substrate should take this effect into account. Such a study is beyond the scope of this paper. In the case of chemisorption, the stress due to W is not the only source of surface stress and the difficulty of a full calculation may be circumvented. The chemical effects of adsorption on the substrate surface atoms (electronic transfer, filling of dangling bonds, etc.) may constitute a major contribution to surface stress as pointed out by Ibach¹ who gave very illustrative examples.^{1,7,8} While

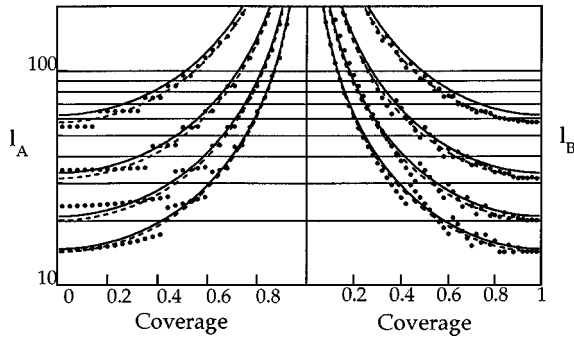


FIG. 3. Variation of l_A and l_B versus coverage for $C_2/C_1 = 0.41, 0.55, 0.74, 1$ (dots from top to bottom). Solid lines are the Marchenko curves and dashed lines are the modified Marchenko curves.

structural studies of Cs adsorbed on Ni(111) have clearly established that the direct forces between adsorbate Cs atoms are repulsive in the whole submonolayer range,⁹ the induced surface stress is tensile and increases quasilinearly with coverage in this range as can be seen on Fig. 6 of Ibach's report.¹ This behavior—tensile surface stress and repulsive direct forces—is a clear, simple, and direct experimental evidence of the little importance of direct adsorbate forces for the value of the effective surface stress. In the case of O adsorbed on Ni(111), similar results are observed and extensive structural studies by Schwennicke *et al.*¹⁰ allow Ibach to estimate the direct adsorbate contribution to the compressive stress to be less than 15%. For attractive direct forces, stress measurements are lacking but we think that the arguments leading to the importance of the “chemical” contribution to surface stress are still valid in chemisorption cases. We, therefore, neglect the dependence of C_2 on l_A .

Since, in the case of chemisorption on a stiff substrate, the Frenkel-Kontorova and Marchenko approaches have compatible basic assumptions, we have then simply to add their two energy terms. We obtain for the energy per unit length:

$$U(L) = U_M(L) + \frac{E_{FK}\left(\frac{L\tau}{a}\right)}{L}. \quad (10)$$

In the case with misfit dislocations, the approximant for E_{FK} [Eq. (8)] does not depend on l_0 . In the absence of dislocations, the asymptotic expression (9) indicates that the main parameter is the ratio l_0/κ . In both the cases, the Frenkel-Kontorova contribution may be written

$$\frac{E_{FK}\left(\frac{L\tau}{a}\right)}{L} = U_0(\tau) - \frac{C_3(\tau L)}{L}. \quad (11)$$

U_0 plays no role in the selection of L . $C_3(\tau L)$ acts as a effective shift of C_1 and therefore yields a τ -dependent correction to κ . Because of the high sensitivity of κ to C_1 exhibited in Eq. (5), the effect of this correction on the resulting pattern may be important.

Let us first examine the state with dislocations. In this case, $C_3(\tau L)$ becomes:

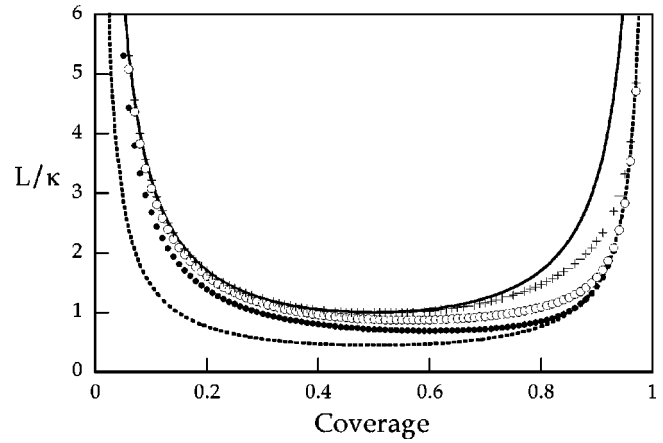


FIG. 4. Variation of L versus coverage for $l_0 a = 0.5\kappa$ (full dots), $l_0 a = \kappa$ (empty dots), $l_0 a = 2\kappa$ (+). The solid line is the Marchenko curve and the dashed line the modified Marchenko curve.

$$C_3(\tau L) = \frac{WP_0}{2\pi} |\sin[\pi\tau L/(aP_0)]|. \quad (12)$$

Figure 3 represents the variations of the adsorbate band size, l_A and the bare substrate band size, l_B versus coverage as obtained by numerical minimization of $U(L)$ for various values of C_2/C_1 , $P_0 = 10$, $W/C_1 = 0.02$. The l_A and l_B curves are “punctuated.” In the l_A curve, these punctuations correspond to quasihorizontal plateaus around odd multiples of $P_0/2$ (minima of E_{FK}/L) separated by discontinuities (branches intersection in E_{FK}/L). The symmetry between l_A and l_B is not preserved, nevertheless a Marchenko behavior given by Eq. (4) with a modified value of κ accounts for the overall l_A and l_B curves

$$\kappa' = 2\pi a \exp\left(1 + \frac{C_1 - WP_0/2\pi}{C_2}\right). \quad (13)$$

Careful study of the variation of the minimum of $U(L)$ with τ shows that the parts of the l_A curves, which correspond to rapid variations between two consecutive plateaus are metastable since a decrease of the energy is obtained by a macroscopic separation into the two self-organized structures corresponding to each plateau. Due to the long range of the elastic Marchenko interactions, a precise determination of the equilibrium patterns would demand to explore solutions corresponding to a microscopic mixing of chains alternatively of length $(2N-1)P_0/2$ and $(2N+1)P_0/2$. This type of solution may lead to a very complex phase diagram as those obtained, for instance, in the anisotropic next-nearest neighbor Ising model.¹¹ While the limited coherence length of realistic surfaces will prevent observations of such complex patterns, the discontinuities in the l_A curve should translate into diffraction peaks broadening for the corresponding coverages. These relative broadenings of ca. 10% may be quite observable, this value being of the same order as the relative width observed by Kern *et al.* in their helium diffraction study of O on Cu(110).¹²

The state with dislocations corresponds to a limited range for the ratio W/C_1 (such that $l_0/P_0 > 2/\pi$). Moreover to use expression (8) for $U_{FK}(L)$, it is necessary that $l_0/P_0 > 2$, i.e., $W/C_1 < (\mu a^2)/(8C_1 P_0^2)$. Both μa^2 and C_1 depend on the adsorbate-adsorbate potential, the former accounting for its

curvature and the latter for its depth. For a van der Waals potential, this ratio is 72, which leads to $W/C_1 < 9/P_0^2$. Adsorbate-adsorbate potential detailed shapes are poorly known but the ratio $(\mu a^2)/C_1$ is a gross feature. The value obtained for the Van der Waals potential may be regarded as providing a reasonable order of magnitude. Values ranging from 20 to 90 are found for various potentials (interatomic potential in diatomic molecules, bimetallic interfaces, gas-atom metal interactions, etc.).^{13,14} Lastly, it is worth noting that in the state with dislocations, the infinite chain ($\tau=1$) necessarily exhibits misfit with the substrate. Therefore, in cases where the complete monolayer is known to be dislocation free, i.e., in registry, the role of the coincidence mesh cannot be invoked to account for patterns at low coverage as was done by Liebsle *et al.* in their study of N on Cu(100).¹⁵

Let us now examine the state without dislocations. We no longer have a full analytic expression for $C_3(\tau L)$ but we know that it vanishes for small L , and its asymptotic behavior for large L is

$$C_{3\infty} = \frac{\mu a^2}{\pi P_0^2} l_0. \quad (14)$$

This asymptotic value of $C_3(\tau L)$ leads to a modified value of κ which takes at large τL , i.e., at high coverage, the value

$$\kappa' = 2\pi a \exp\left(1 + \frac{C_1 - C_{3\infty}}{C_2}\right). \quad (15)$$

The previous discussion of W/C_1 is also relevant to $C_{3\infty}/C_1$. For a van der Waals potential, this ratio must obey the relations

$$\frac{C_{3\infty}}{C_1} = \frac{\mu a^2}{C_1} \frac{l_0^2}{P_0^2} \frac{1}{\pi l_0} < \frac{288}{\pi^3 l_0} \approx \frac{9}{l_0}. \quad (16)$$

Figure 4 exhibits L/κ versus coverage for $l_0=5$, $P_0=10$, and various values of $(l_0 a)/\kappa$. For legibility, we have chosen a rather high ratio $C_{3\infty}/C_1=0.8$. It clearly appears that the L curve evolves smoothly, with increasing coverage, from the $\kappa/\sin(\pi\tau)$ curve to the $\kappa'/\sin(\pi\tau)$ one.

Taking into account the Frenkel-Kontorova energy in the state without dislocations is clearly seen to break the Marchenko $\tau \rightarrow 1 - \tau$ symmetry. Indeed, this mechanism leads to relaxations which depend on the chain size and may significantly modify the effective boundary energy. We believe that this effect is a good candidate to explain some discrepancies between the Marchenko prediction and experimental results about O on Cu(110).^{16,12}

In conclusion, we have shown that in a chemisorption case, the contribution of the Frenkel-Kontorova mechanism to the energy suppresses the symmetry of Marchenko results. In the state with misfit dislocations, adsorbate band size corresponding to odd half multiples of the coincidence mesh are favored, and the period variation with coverage is punctuated. More surprisingly, in the state with no dislocations, the Marchenko symmetry is not preserved due to short-range interactions between the edges of an adsorbate domain. These two results are due to an important dependence of local relaxations on adsorbate band size; this dependence should lead to similar but more complex results for other auto-organized systems such as vicinal faces or bare substrates with anisotropic stress.³

We would like to thank J. Barnard, P. Nozières, and P. Zeppenfeld for discussions and C. Caroli for support.

¹H. Ibach, Surf. Sci. Rep. **29**, 193 (1997).

²V.I. Marchenko, Zh. Éksp. Teor. Fiz. **81**, 1141 (1981) [Sov. Phys. JETP **54**, 605 (1981)].

³O.L. Alerhand, D. Vanderbilt, R.D. Meade, and J.D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).

⁴Y.J. Frenkel and T. Kontorova, Zh. Eksp. Teor. Fiz. **8**, 340 (1938).

⁵F.C. Frank and J.H. van der Merwe, Proc. R. Soc. Ser. A **198**, 205 (1949).

⁶W.A. Jesser and J.H. van der Merwe, Surf. Sci. **31**, 229 (1972).

⁷A. Grossmann, Thesis, RWTH Aachen D80, 1996.

⁸A. Grossmann, W. Erley, and H. Ibach, Surf. Sci. **337**, 183 (1995).

⁹S. Chandavarkar, R.D. Diehl, A. Faké, and J. Jupille, Surf. Sci. **211/212**, 432 (1989).

¹⁰C. Schwennicke and H. Pfnür, Surf. Sci. **369**, 248 (1996).

¹¹P. Bak, Rep. Prog. Phys. **45**, 587 (1982).

¹²K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. Goerge, and G. Comsa, Phys. Rev. Lett. **67**, 855 (1991).

¹³J. Ferrante, J.R. Smith, and J.H. Rose, Phys. Rev. Lett. **50**, 1385 (1983).

¹⁴J.H. Rose, J.R. Smith, and J. Ferrante, Phys. Rev. B **28**, 1835 (1983).

¹⁵F.M. Leiblse, S.S. Dhesi, S.D. Barret, and A.W. Robinson, Surf. Sci. **317**, 309 (1994).

¹⁶D. Vanderbilt, Surf. Sci. Lett. **268**, L300 (1992).