

Microscopic model for dimer buckling on Si(001)

Frank H. Stillinger

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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Examination of scanning tunneling microscopy (STM) images for the dimerized Si(001) surface, particularly at low temperature, suggests that dimers can exist in either a buckled or an unbuckled geometry, with both mechanically stable but the former lower in energy. A simple model for such behavior has been constructed. Each dimer is represented by a single angular degree of freedom (“tipping” angle). Interactions couple dimers nonlinearly to their nearest neighbors, and linearly to surface defects. The system potential energy has a simple algebraic form in the angles. Stable tipping patterns have been computed, and conform to the qualitative features of STM observations. The model should facilitate study of possible surface phase transitions on Si(001) by conventional computer-simulation methods.

I. INTRODUCTION

While the existence of dimers on the Si(001) surface experimentally is a long-established fact,¹⁻⁵ details of their geometry have been a source of continuing disagreement.⁶ In particular, no consensus has been reached concerning (a) whether the stable form for a dimer involves a bond parallel to the surface, or a tipped bond (“buckled dimers”); and (b) if stable tipping obtains, what surface pattern of tipping angles yields the lowest energy. Theoretical calculations motivated by the desire to resolve these ambiguities⁷⁻¹¹ unfortunately have had the contrary effect, by creating their own uncertainties and disagreements.

Recently, Wolkow¹² has obtained some remarkable scanning tunneling microscopy (STM) images of dimerized Si(001) surfaces over a substantial temperature range. Observing these images invites the following conclusions.

(1) Buckled dimers are indeed the lowest energy configuration, but various excitation processes (including thermal excitation around room temperature) can produce rows of untipped dimers.

(2) Pairs of neighboring buckled dimers along a row (i.e., in the surface direction perpendicular to the dimer bonds) have strongly anticorrelated tipping angles; pairs of neighboring dimers in two successive rows are weakly anticorrelated.

(3) The Si(001) surfaces inevitably contain a significant density of structural defects. These defects couple strongly to the dimer buckling and thus influence the observed patterns.

With regard to (a) above, it ironically appears that both “buckled” and “unbuckled” dimers may contribute in the correct solution.

This paper proposes and investigates some aspects of a simple model to describe and to rationalize the STM observations. Section II presents the model, while Sec. III provides some illustrative numerical calculations. Conclusions and discussion appear in Sec. IV.

II. DIMER BUCKLING MODEL

The Si(001) surface of interest will have N dimers, arranged in a pattern with rectangular symmetry, whose state of tipping will be described by a set of angles α_i ($i=1, \dots, N$). Figure 1 illustrates the dimer arrangement. A common rotation sense will apply to all of these angles, and an untipped dimer has $\alpha_i=0$. The objective is to identify a physically reasonable potential-energy function $\Phi(\alpha_1, \dots, \alpha_N)$ that describes interactions of the dimers with the substrate and among themselves. Clearly the form chosen for Φ must be consistent with substrate symmetry; if no defects are present then

$$\Phi(\alpha_1, \dots, \alpha_N) = \Phi(-\alpha_1, \dots, -\alpha_N). \tag{2.1}$$

To begin, it is useful to recall the quartic anharmonic function:

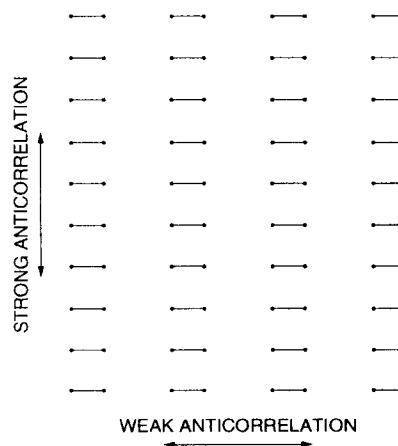


FIG. 1. Dimer pattern on the Si(001) surface. No tipping is indicated, but would involve one end of the dimer moving up out of the drawing, the other end downward. The directions of strong and of weak tipping anticorrelation are shown, as suggested by STM observations (Ref. 12).

$$f(\alpha, B) = \alpha^4 + B\alpha^2, \quad (2.2)$$

where B is a parameter. If $B \geq 0$ this function of α possesses only a single minimum, at $\alpha = 0$. However, if $B < 0$, f develops a pair of minima flanking the origin, at

$$\alpha = \pm(-B/2)^{1/2}. \quad (2.3)$$

The STM observations suggest that both untipped and tipped dimers can be locally stable, conditions permitting. Therefore it seems desirable to have the model automatically incorporate both of these cases by employing Eq. (2.2) with B 's of variable sign.

In the absence of defects, the following generic form for Φ will be adopted:

$$\Phi = \sum_{i=1}^N f(\alpha_i, B_i) + \Phi_{\text{int}}. \quad (2.4)$$

Here B_i will depend on the collection of dimer angles in the vicinity of dimer i , and will thereby be capable of changing sign. Interactions between dimers will be comprised partly in Φ_{int} , the task of which is to induce the observed neighbor anticorrelations. For simplicity the specific forms assigned to B_i and Φ_{int} are elementary algebraic functions:

$$B_i = -2 + K \sum_{j=1}^N l(i, j)(\alpha_j^2 - \lambda^2)^2, \quad (2.5)$$

$$\Phi_{\text{int}} = -\frac{1}{2}J \sum_{i, j=1}^N (-1)^{s(i, j)} l(i, j) \alpha_i \alpha_j, \quad (2.6)$$

where J , K , and λ are positive constants. The symbol $s(i, j)$ represents the minimum integer number of steps that must be taken (either along a row of dimers or between rows) to go from dimer i to dimer j . The range of interactions between dimers is described by $l(i, j)$ for which it will be supposed

$$\begin{aligned} l(i, i) &= 0, \\ l(i, j) &\geq 0, \\ \sum_j l(i, j) &= 1. \end{aligned} \quad (2.7)$$

This pair function will convey surface anisotropy.

Notice that if all $\alpha_j = \pm\lambda$ with the single exception of dimer angle α_i , the corresponding B_i would equal -2 . Hence, if Φ_{int} did not matter, dimer i would also prefer to tip (in either direction). Contraiwise, sets of α_j 's differing substantially from $\pm\lambda$ would give positive contributions to the sum in Eq. (2.5); and if K were sufficiently large B_i would be positive. In this latter circumstance $\alpha_i = 0$ would be preferred (again if Φ_{int} did not matter).

The interdimer interactions represented by the B_i , Eq. (2.5), are insensitive to the signs of the tipping angles. By contrast, Φ_{int} in Eq. (2.6) depends on relative signs and will be minimized when nearest neighbors in both surface directions are tipped out of phase.

Detailed information is not yet available about the nature of surface defects. These might include adatoms, substitutional impurities, missing dimers, and shallow

bonding defects. In addition the dimers can be expected to interact with nearby ledges. As an interim measure it is attractive to suppose that each angular degree of freedom α_i couples linearly to the defects with its own coupling constant g_i . Consequently the generalization of Eq. (2.4) to include defects is postulated to be

$$\Phi = \sum_{i=1}^N [f(\alpha_i, B_i) + g_i \alpha_i] + \Phi_{\text{int}}. \quad (2.8)$$

There should be no sign preference among the g_i , and only those for dimers near to defects will differ substantially from zero. For present purposes it will be assumed that no dimers are missing, though this type of surface defect certainly can be accommodated by a trivial extension of the model.

Unfortunately, STM measurements cannot yet determine absolute magnitudes of tipping angles. Comparisons with models such as that advocated here will thus temporarily have to be confined to qualitative characteristics of surface patterns.

III. NUMERICAL CALCULATIONS

To illustrate some simple aspects of the model, it is useful to observe first the collective behavior of Φ as all angles vary together. For simplicity, coupling to defects initially will be disregarded. If all angles have the same magnitude, but nearest neighbors tip in opposite directions, we can set

$$\alpha_i = (-1)^{s(1, i)} \alpha \quad (i = 1, \dots, N). \quad (3.1)$$

Then the resulting potential energy per dimer Φ/N , regarded as a function of α , has the form

$$\phi_-(\alpha) = K\alpha^6 + (1 - 2K\lambda^2)\alpha^4 + (K\lambda^4 - \frac{1}{2}J - 2)\alpha^2. \quad (3.2)$$

The opposite situation (in-phase tipping) would have all $\alpha_i = \alpha$ ($i = 1, \dots, N$), and yields

$$\phi_+(\alpha) = K\alpha^6 + (1 - 2K\lambda^2)\alpha^4 + (K\lambda^4 + \frac{1}{2}J^* - 2)\alpha^2, \quad (3.3)$$

where

$$J^* = -J \sum_{j=1}^N (-1)^{s(i, j)} l(i, j). \quad (3.4)$$

Note that if $l(i, j)$ were nonvanishing only for nearest neighbors either along a row or in neighboring rows, then $J = J^*$.

Figure 2 presents plots of ϕ_- and ϕ_+ vs α for the choice of parameters

$$J = J^* = 2.2, \quad K = 1.0, \quad \lambda = 1.6. \quad (3.5)$$

Both functions exhibit local minima at $\alpha = 0$, where all dimers are in an untipped state. A pair of deep flanking minima appear in ϕ_- :

$$\phi_-(\alpha = \pm 1.49351) = -1.697253818, \quad (3.6)$$

which correspond to the lowest attainable potential energy for the parameter set (3.5). A pair of extremely shallow minima also appear in ϕ_+ at the positions

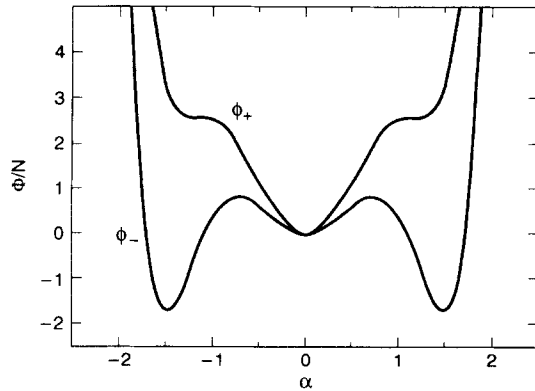


FIG. 2. Variations of potential energy per dimer as all dimers tip together in the same direction (ϕ_+) or in alternating directions (ϕ_-). The curves refer to the parameter set (3.5).

$$\phi_+(\alpha = \pm 1.18836) = 2.583824443, \quad (3.7)$$

but these are indistinguishable from horizontal inflection points in Fig. 2, and should have little structural significance. A slightly larger J would eliminate these minima altogether.

Examination of ϕ_- and ϕ_+ curves alone does not guarantee that the totally untipped dimer configuration is stable against arbitrary small deformations. However the appropriate checks have been carried out, and indeed this configuration is a legitimate metastable state for the parameter set (3.5). Thus the basic requirements imposed on the model by the STM observations have been satisfied, at least for the chosen parameter set.

Further study of the model requires that pair function $l(i, j)$ be specified. The most obvious choice is that it be nonvanishing only for nearest-neighbor dimer pairs. In view of the surface anisotropy, we can write

$$l(i, j) = \begin{cases} \frac{1}{2}(1 - \epsilon) & (\text{along rows}), \\ \frac{1}{2}\epsilon & (\text{between rows}). \end{cases} \quad (3.8)$$

Parameter ϵ controls anisotropy, and is expected to lie in the range $0 < \epsilon < \frac{1}{2}$ to provide stronger tipping anticorrelation along rows than between rows, as Fig. 1 indicates. Notice that the normalization condition in (2.7) is automatically satisfied.

Careful examination of a large collection of STM images should help to determine a reasonable range for the anisotropy parameter ϵ . In particular, one might search for occurrence of single rows of essentially untipped dimers residing stably between left- and right-hand side rows that are tipped in the same alternating pattern. In this connection, consider the hypothetical tipping pattern shown in Fig. 3, which is assumed to extend arbitrarily far in both directions. Rows alternate between weak and strong tipping, with nearest neighbors anticorrelated both along and between rows. No defects are present. Let α and β represent, respectively, the tipping angle magnitudes in the weakly and strongly tipped rows. Then the energy per dimer $\phi = \Phi/N$ depends on α and β

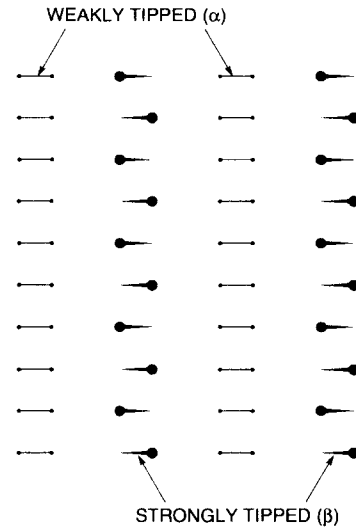


FIG. 3. Alternating rows of weakly and strongly tipped dimers. Angles α and β represent the respective tipping magnitudes. All nearest-neighbor pairs tip in opposite directions.

in the following way:

$$\begin{aligned} \phi(\alpha, \beta) = & \frac{1}{2}[\alpha^4 + \beta^4 + B(\alpha, \beta)\alpha^2 + B(\beta, \alpha)\beta^2] \\ & - \frac{1}{4}J[(1 - \epsilon)(\alpha^2 + \beta^2) + 2\epsilon\alpha\beta], \end{aligned} \quad (3.9)$$

where

$$B(\alpha, \beta) = -2 + K[(1 - \epsilon)(\alpha^2 - \lambda^2)^2 + \epsilon(\beta^2 - \lambda^2)^2]. \quad (3.10)$$

The last expression has been minimized numerically with respect to α and β , for various values of ϵ . Once again the parameter set (3.5) has been invoked for illustration. Results are displayed in Fig. 4. Solutions with $0 \leq \alpha < \beta$ can be found only if

$$0 \leq \epsilon \lesssim 0.148; \quad (3.11)$$

for large ϵ (less anisotropy) only the uniform solution ex-

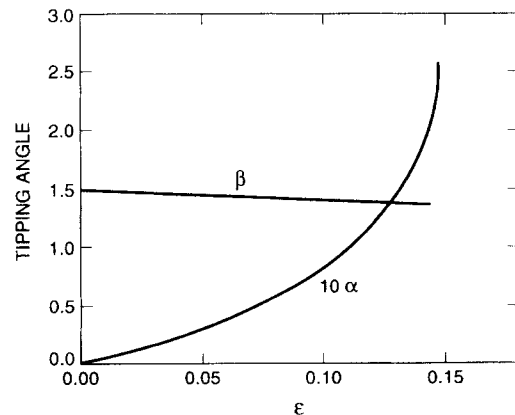


FIG. 4. Stable pairs of tipping-angle magnitudes vs anisotropy parameter ϵ . These refer to the pattern in Fig. 3, and were obtained by minimizing expression (3.9).

ists, with $\alpha = \beta$ numerically equal to the value displayed earlier in Eq. (3.6).

The consequences of coupling to defects will now briefly be considered. It was mentioned above that an everywhere-untipped pattern of dimers represents a metastable (i.e., relative) minimum of Φ , in the absence of defects. Coupling even a single dimer to the defect field in a sea of untipped dimers has the effect of creating a local island of anticorrelated tipping. Table I provides a numerical illustration, showing tipping angle values for the perturbed- Φ relative minimum in the vicinity of a dimer (identified by the box) for which

$$g_i = -10.0. \quad (3.12)$$

As before, the parameters in Eq. (3.5) apply, along with the anisotropy

$$\varepsilon = 0.11. \quad (3.13)$$

Notice the relatively slow rate of decay of tipping angles along the row containing the coupled dimer. This feature seems to be qualitatively in accord with Wolkow's observations.¹² While we cannot accurately gauge the tipping angles on real Si(001) surfaces, it seems to be a reasonable supposition that the threshold of observable tipping is roughly $\frac{1}{20}$ of the maximum (i.e., $|\alpha_i| \cong 0.08$). If this is so, then the range of observable perturbation for results in Table I is about nine dimers along the row, but imperceptible in the neighboring rows.

The results reported in Table I were obtained by steepest-descent relaxation on the Φ hypersurface in the space of $\alpha_1, \dots, \alpha_N$ starting from the totally untipped state. The specific calculation involved 10 rows each of 24 dimers ($N = 240$). Periodic boundary conditions were imposed in both surface directions.

Numerical details of the "anticorrelation island" displayed in Table I are quite sensitive to surface anisot-

TABLE I. Tipping angles near an isolated defect, embedded in an otherwise unbuckled-dimer surface. Parameter values: $\varepsilon = 0.11$; $J = 2.2$; $K = 1.0$; $\lambda = 1.6$. The single dimer indicated by the box is defect coupled, with $g_i = -10.0$. Results shown are the central portion of an $N = 240$ system (10 rows of 24 dimers), to which periodic boundary conditions apply.

0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.004	0.000	0.000
0.000	0.001	-0.037	0.001	0.000
0.000	-0.006	0.305	-0.006	0.000
0.000	0.017	-0.888	0.017	0.000
0.000	-0.026	1.246	-0.026	0.000
-0.001	0.032	-1.405	0.032	-0.001
0.001	-0.037	1.592	-0.037	0.001
-0.001	0.032	-1.405	0.032	-0.001
0.000	-0.026	1.246	-0.026	0.000
0.000	0.017	-0.888	0.017	0.000
0.000	-0.006	0.305	-0.006	0.000
0.000	0.001	-0.037	0.001	0.000
0.000	0.000	0.004	0.000	0.000
0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000

ropy. If ε is decreased to 0.10, other parameters unchanged, tipping angles do not decay to zero away from the defect location, but instead produce long-range tipping order along the entire row, with α_i approaching ± 1.4211 far from the defect.

The interaction between a pair of defect-coupled anticorrelation islands along the same row can produce a string of intervening strongly buckled dimers. Table II offers an example, using the same parameter set as for Table I. The defect coupling constants g_i have the same magnitude as before, -10.0 ; they act on dimers eight neighbor spacings apart along the row. Evidently there is no limit on the length of such a string.

The results presented in Tables I and II are among the simplest possibilities. It is clear that realistic distributions of defects corresponding to observed surface imperfections¹² can produce quite elaborate patterns of tipping angles at the various relative minima of the potential energy function $\Phi(\alpha_1, \dots, \alpha_N)$.

It should be mentioned in passing that metastable tipping imperfections can exist even in the absence of coupling g_i , at least when parameters (3.5) and (3.13) apply. If the surface is essentially everywhere in its lowest-energy, strongly tipped state ($\alpha_i = \pm 1.4935$), a single dimer can be tipped in the "wrong" sense (going from ± 1.4935 to ∓ 1.3456) with only a minor effect on the angles of its immediate neighbors. However the barrier is apparently quite low for de-excitation of this local imperfection.

IV. CONCLUSIONS AND DISCUSSION

By attributing a single angular degree of freedom to each dimer on the Si(001) surface, a model has been con-

TABLE II. Tipping angles near a pair of mutually reinforcing defects, embedded in an otherwise unbuckled dimer surface. Conditions identical to those of Table I, except there are two defect-coupled dimers (boxes) with $g_i = -10.0$.

0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.004	0.000	0.000
0.000	0.001	-0.037	0.001	0.000
0.000	-0.006	0.309	-0.006	0.000
0.000	0.017	-0.891	0.017	0.000
0.000	-0.026	1.248	-0.026	0.000
-0.001	0.032	-1.406	0.032	-0.001
0.001	-0.037	1.595	-0.037	0.001
-0.001	0.034	-1.440	0.034	-0.001
0.001	-0.032	1.417	-0.032	0.001
-0.001	0.032	-1.413	0.032	-0.001
0.001	-0.032	1.412	-0.032	0.001
-0.001	0.032	-1.413	0.032	-0.001
0.001	-0.032	1.417	-0.032	0.001
-0.001	0.034	-1.440	0.034	-0.001
0.001	-0.037	1.595	-0.037	0.001
-0.001	0.032	-1.406	0.032	-0.001
0.000	-0.026	1.248	-0.026	0.000
0.000	0.017	-0.891	0.017	0.000
0.000	-0.006	0.309	-0.006	0.000
0.000	0.001	-0.037	0.001	0.000
0.000	0.000	0.004	0.000	0.000
0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000

structed to describe the observed patterns of tipping. The interaction potential in the model has a simple algebraic format, and includes linear coupling to defects. A key feature is the presence (at least for some parameter choices) of mechanically stable dimer arrangements exhibiting both tipped and untipped dimers. This characteristic distinguishes the present model from at least some others that have been advanced.¹³ First indications show that the model conforms at least qualitatively to STM observations.¹²

The model currently contains four scalar parameters (J, K, λ , and ϵ) whose magnitudes cannot yet be precisely assigned. Furthermore the linear coupling constants g_i for defects are speculative. It would be extremely valuable to have sets of high-accuracy quantum-mechanical calculations for the dimerized Si(001) surface whose results fix these parameters. But even before such information becomes available it is useful to have established the

existence of a scenario in which tipped and untipped dimers can coexist stably. This last point has been a major objective in the present work.

The possibility of one or more surface-pattern phase transitions is a fascinating open problem. The model proposed here is well suited for computer simulation by either the Monte Carlo¹⁴ or the molecular-dynamics¹⁵ approach, and in this way could be exhaustively analyzed for its equilibrium phase behavior for various sets of parameters. The results could then be compared against standard analytic approximations in the statistical mechanical theory, the most obvious of which is the so-called "mean-field theory."¹⁶

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¹R. E. Schlier and H. E. Farnsworth, *J. Chem. Phys.* **30**, 917 (1959).

²J. J. Lander and J. Morrison, *J. Chem. Phys.* **37**, 729 (1962).

³T. D. Poppendieck, T. C. Ngoc, and B. M. Webb, *Surf. Sci.* **75**, 287 (1978).

⁴M. J. Cardillo and G. E. Becker, *Phys. Rev. Lett.* **40**, 1148 (1978).

⁵M. J. Cardillo and G. E. Becker, *Phys. Rev. B* **21**, 1497 (1980).

⁶R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev. B* **34**, 5343 (1986).

⁷D. J. Chadi, *Phys. Rev. Lett.* **43**, 43 (1979).

⁸E. Artacho and F. Yndurain, *Phys. Rev. Lett.* **62**, 2491 (1989).

⁹K. Pandey, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors*, edited by D. J. Chadi and W. A. Harrison (Springer-Verlag, New York,

1985), p. 55.

¹⁰M. C. Payne, N. Roberts, R. J. Needs, M. Needels, and J. D. Joannopoulos, *Surf. Sci.* **211**, 1 (1989).

¹¹N. Roberts and R. J. Needs, *Surf. Sci.* **236**, 112 (1990).

¹²R. A. Wolkow, *Phys. Rev. Lett.* **68**, 2636 (1992).

¹³G. P. Kochanski and J. E. Griffith, *Surf. Sci. Lett.* **249**, L293 (1991).

¹⁴J. P. Valleau and S. G. Whittington, in *Statistical Mechanics, Part A: Equilibrium Techniques*, edited by B. J. Berne (Plenum, New York, 1977), Chap. 4.

¹⁵*Molecular Dynamics Simulation of Statistical-Mechanical Systems*, edited by G. Ciccotti and W. G. Hoover (North-Holland, Amsterdam, 1986).

¹⁶S.-K. Ma, *Statistical Mechanics* (World Scientific, Philadelphia, 1985), Chap. 27.