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Attractive interactions between steps

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Motivated by recent scanning-tunneling-microscopy results for vicinal copper surfaces by Ibach and co-workers, we consider theoretically possible sources of *attractive* interactions between monatomic height steps on crystal surfaces. For steps with a mean separation of l, a mechanism driven by surface-stress relaxation in the vicinity of each step can, in some circumstances, lead to an attractive interaction which varies as l^{-2}. An alternative indirect mechanism mediated by conduction electrons leads to an oscillatory interaction energy which decays as $l^{-9/2}$. The relevance of these model calculations to real materials is discussed.

In a recent paper by Frohn *et al.*,[1] scanning-tunneling-microscopy images of a sequence of carefully prepared and equilibriated surfaces vicinal to Cu(100) were presented and interpreted in a manner that strongly suggests the presence of an effective *attractive* interaction between monatomic height steps for step separations l of the order of 3–5 atomic spacings. Attractive interactions between steps (varying as l^{-1}) also have been invoked[2] to rationalize the observed[3] equilibrium shape of small gold crystallites in the vicinity of its (111) facets. Since the existence of such forces also has implications for theories of surface phase transitions,[4,5] thermal step wandering,[6] and the kinetics of step motion,[7–9] it seems appropriate to critically examine various speculations regarding their physical origin in greater detail. That is the purpose of this paper.

For the case of ionic crystals, the existence of attractive electrostatic interactions between steps was recognized already in the work of Kossel[10] and Stranski[11] on the terrace-step-kink model of vicinal surfaces. For metal surfaces, steps exhibit no net charge but a dipole moment can occur due to the spillout of the electron-density distribution in the vicinity of the step.[12,13] In that case, the energy of interaction between two steps is[14]

$$U(l)=\frac{2\mathbf{p}_1\cdot\mathbf{p}_2-4(\mathbf{p}_1\cdot\mathbf{n})(\mathbf{p}_2\cdot\mathbf{n})}{l^2} \tag{1}$$

per unit length of step where $\mathbf{p}_1$ and $\mathbf{p}_2$ are the dipole moments of the step-charge distributions and $\mathbf{n}$ is a unit vector which points from $\mathbf{p}_1$ to $\mathbf{p}_2$, i.e., parallel to the plane of the vicinal surface. Assuming that $\mathbf{p}_1=\mathbf{p}_2$, this interaction becomes attractive when the angle between each dipole and the normal to the vicinal surface exceeds 45°. As pointed out by Frohn *et al.*,[1] a collective rotation of two adjacent dipoles can occur to take advantage of this energy gain even if the dipole moment associated with an isolated step is oriented close to the normal.

Blakely and Schwoebel[15] demonstrated long ago that surface stress[16] can drive atomic relaxations in the vicinity of steps which, in turn, induce elastic distortions in the bulk. For a surface in the x-y plane with steps running parallel to the y axis, the latter yield an interaction energy per unit length of step which takes the form[17]

$$U(l)=2\frac{1-\sigma^2}{\pi E}\frac{\mathbf{f}_1\cdot\mathbf{f}_2}{l^2} \tag{2}$$

within linear elasticity theory. In this expression, σ and E denote the Poisson ratio and Young's modulus of the solid and the vectors $\mathbf{f}_1$ and $\mathbf{f}_2$ lie in the x-z plane with the x component (z component) equal to the g_{xx} (g_{xx}) element of the surface-stress tensor associated with the step.[17] One observes immediately[18] that the interaction energy (2) is strictly repulsive on a vicinal surface when $\mathbf{f}_1=\mathbf{f}_2$. However, it is possible to imagine a symmetry-breaking situation in which the atomic distortions near alternate steps differ in such a way that the elastic force becomes attractive. This could happen if, for example, a reconstruction occurred so that the surface stress of the terrace between two closely spaced steps switched from compressive to tensile (or vice versa). Given the well-known resistance of metals to reconstruction,[19] this scenario most likely would occur (if at all) on semiconductor surfaces.[5] On the other hand, a similar effect could occur on metal surfaces where the electric dipoles $\mathbf{p}_1$ and $\mathbf{p}_2$ in (1) reorient into different directions. If this symmetry breaking is large enough, an attractive interaction can result.

An alternative mechanism for producing an attraction between steps by atomic relaxations has been proposed by Yamamoto and Izuyama[20] in order to justify the theoretical analysis[2] of the gold crystallite data noted earlier. They postulate an expression for the surface energy per unit area of surface of the form

$$f(\theta,Q)=f_0+(\varepsilon_0+\alpha Q)|\theta|+w|\theta|^3+\tfrac{1}{2}KQ^2\ . \tag{3}$$

Here, f_0 is the surface energy of the flat (111) surface, θ is the *average* miscut of the vicinal surface, Q is the magnitude of a (rigid) relaxation of the outermost surface plane, and K is an elastic constant. The repulsive cubic term may be taken to represent either the conventional elastic repulsion discussed above and/or the contribution to the free energy from the entropy of the steps;[20] both are dipolar.[21] The physical idea is that the net creation energy of an isolated step is imagined to depend on the relaxation Q. The final term in (3) is the elastic cost of the relaxation away from the step. By minimizing $f(\theta,Q)$ with respect to Q, one sees that an attractive interaction proportional to θ^2 results. The concomitant self-consistent solution for Q reflects a communication between steps that goes beyond the simple superposition of strain fields assumed in linear elasticity theory.

Unfortunately, this explanation is incorrect because the assumption of a rigid relaxation is unphysical. In the central region of a terrace between two widely separated steps, the magnitude of the relaxation must return to the value obtained for the perfectly flat surface independent of its magnitude in the immediate vicinity of a step.[22] Both terms in the free-energy expression (3), which depend upon Q, are inconsistent with this fact. It is natural, then, to ask whether a simple model free energy can be constructed that captures the inhomogeneous nature of lattice relaxation on a vicinal surface. To do so, let Q denote instead the magnitude of a collective coordinate that describes the lattice relaxation in the vicinity of a single step. For an isolated step, $Q=0$ since ε_0 denotes the totally relaxed energy of such a step. Then, an appropriate replacement for (3) is

$$f(\theta,Q)=f_0+(\varepsilon_0+\tfrac{1}{2}KQ^2)|\theta|+w|\theta|^3+Q|\theta|^p\ , \qquad (4)$$

where the term quadratic in Q counts the elastic strain energy incurred (per step) if the relaxation deviates from that of widely separated steps, i.e., zero. The final term accounts for the presumed nonlinear interaction suggested above. Since this communication can only be effected by atomic displacements, which fall off inversely with distance from a step, the exponent p can be no smaller than 2. Minimizing (4) with respect to Q, one finds

$$f(\theta)=f_0+\varepsilon_0|\theta|+w|\theta|^3-\beta|\theta|^{2p-1}\ . \qquad (5)$$

Thus, at best ($p=2$) one obtains an attractive inverse square[21] interaction which renormalizes the coefficient w in (5). Although w could be driven negative, there is reason to suppose that this nonlinear effect is quite small, at least for metals. Evidence for this comes from atomistic simulations of step relaxations on vicinal Al surfaces performed by Chen and co-workers[23,24] using a realistic embedded-atom-type energy functional. There, one observes that the magnitude of the relaxation in the vicinity of a step does *not* vary as the step separation varies.

Finally, we consider the interaction between steps on a metal surface that results from the electronic screening by conduction electrons of the perturbation in the periodic ion potential associated with the presence of each step. As suggested by Frohn *et al.*,[1] this is expected to lead to an oscillatory Friedel-type interaction that will be attractive at some distances. To rationalize this expectation, recall first the results of Einstein[25] and Lau and Kohn[26] for the interaction energy between two adatoms weakly adsorbed onto a flat substrate separated by a large distance l:

$$E_{\text{int}} \sim \frac{1}{l^m}\cos(2k_F l)\ . \qquad (6)$$

The exponent m is equal to 5 for the simplest case where the Fermi energy does not lie in a surface band. Now consider the case of two parallel rows of atoms weakly adsorbed on a flat substrate and separated by a distance l. To lowest order in the intrarow coupling, the interaction energy between the rows can be computed by simply summing the above atom-atom interaction over all atoms in each row. For small k_F, one finds the asymptotic (large l) result

$$E_{\text{int}} \sim \frac{1}{l^{m-1/2}}\cos\left[2k_F l+\frac{\pi}{4}\right]\ . \qquad (7)$$

Note that the interaction falls off more slowly than the atom-atom interaction by a factor of $\sqrt{l}$.

Of course, (7) is the energy of two rows, not two steps. However, with the same weak-coupling assumptions, one can find the interaction between, say, an up step and a down step by summing over all rows in the half planes that constitute the terraces bounded by the steps [Fig. 1(a)]. For most values of k_F, the result is again (7) (apart from a change of overall sign) because of partial cancellations arising from the oscillatory nature of the integrand. For large values of k_F very near the Brillouin-zone boundary, such cancellations need not occur; the step-step interaction is still oscillatory, but may fall off with a smaller power of l.

The foregoing is suggestive, but not completely correct, since the bonds involving atoms on the terraces are not weak but, in fact, are of strength comparable to bulk bonds. To address this question, we turn to a more rigorous computation for the case of the interaction between one row of adatoms and one missing row of atoms [Fig. 1(b)]. We consider a single-s-band tight-binding model for a cubic crystal and adopt the convention of Einstein,[25] whereby the lattice constant is set to unity, the

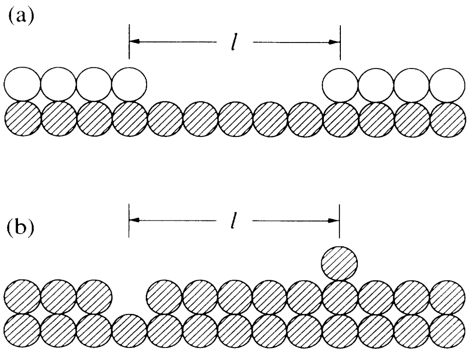

FIG. 1. Side view of a surface with (a) an up step and a down step which bound two semi-infinite terraces of a weakly bonded material adsorbed onto a substrate; (b) an extra row of atoms and a missing row of atoms relative to a flat substrate surface.

on-site energy is set to zero, and the hopping parameter that connects nearest neighbors is set to $\frac{1}{2}$ to fix the scale of energy. The essential ingredient required to compute the interaction is the surface Green function.[27] In a basis periodic along the atomic rows (y direction) and localized in the orthogonal x direction, this quantity takes the asymptotic form

$$G_{ol}(E,k_y) = -\left[\frac{2}{\pi}\sin x_0\right]^{1/2} \frac{1}{l^{3/2}} \exp(ilx_0+\pi/4) \ , \tag{8}$$

where $\cos x_0 = 1+E-\cos k_y$ and, for simplicity, we assume that the Fermi energy lies within the bottom third of the band: $-3<E_F<-1$.

Slightly generalizing the methodology of Einstein,[28] we find an interaction energy

$$E_{\text{int}} = -\frac{1}{2\pi}\int_{-\infty}^{E_F} \text{Tr}\,\text{Im}\,G_{ol}^2 \frac{\bar{G}_{aa}}{G_{oo}}\,dE \ , \tag{9}$$

where

$$\bar{G}_{aa} = \frac{G_{aa}}{1-G_{aa}G_{oo}/4} \tag{10}$$

and $G_{aa}(k_y,E)$ is the Green function for a single row of atoms. Apart from a prefactor, E_{int} can be evaluated for large l with the result

$$E_{\text{int}} \sim \frac{1}{l^{9/2}} \cos[2l\cos^{-1}(2+E_F)+\pi/4] \ . \tag{11}$$

Note that this falls off with the same power of distance as the earlier weak-coupling prediction. Unfortunately, we cannot easily extend this calculation to the most interesting case of two steps on a vicinal surface because the corresponding perturbation is not localized in any simple basis set. On the other hand, the argument used above for weak-coupling plausibly suggests that the true step-step interaction will still have this form. Indeed, the stronger bonding in the present case seems particularly likely to produce screening of more distant row-missing row interactions [cf. Fig. 1(a)] resulting in a net result quite similar to (11). Of course, this is not definitive. A more complete electronic-structure calculation clearly would be desirable to test this prediction.

In summary, we have examined a number of different mechanisms capable of producing a net attractive interaction between steps on a vicinal surface. Direct nonelectronic processes generally require a symmetry-breaking distortion of the surface to be effective but these appear less likely on metal surfaces than the indirect electronic interaction explored above. Extensive measurements for the corresponding adsorbate-adsorbate problem[29] demonstrate that the range and energy scale of the phenomenon is compatible with the observations of Frohn *et al.*[1]

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[1] J. Frohn, M. Giesen, M. Poensgen, J. F. Wolf, and H. Ibach, Phys. Rev. Lett. **67**, 3543 (1991).

[2] J. J. Sáenz and N. Garcia, Surf. Sci. **155**, 24 (1985).

[3] J. C. Heyraud and J. J. Métois, J. Cryst. Growth **50**, 571 (1980); Acta Metall. **28**, 1789 (1980).

[4] H. van Beijeren and I. Nolden, in *Structure and Dynamics of Surfaces II*, edited by W. Schommers and P. von Blanckenhagen (Springer-Verlag, Berlin, 1987), pp. 259–300.

[5] See, e.g., E. Pehlke and J. Tersoff, Phys. Rev. Lett. **67**, 1290 (1991), and references therein.

[6] N. C. Bartelt, T. L. Einstein, and E. D. Williams, Surf. Sci. Lett. **240**, L591 (1990).

[7] A. Rettori and J. Villain, J. Phys. (Paris) **49**, 257 (1988).

[8] M. Uwaha, J. Phys. Soc. Jpn. **57**, 1681 (1988).

[9] M. Ozdemir and A. Zangwill, Phys. Rev. B **42**, 5013 (1990).

[10] W. Kossel, Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl. 135 (1927).

[11] I. Stranski, Z. Phys. Chem. (Leipzig) **136**, 259 (1928).

[12] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).

[13] M. D. Thompson and H. B. Huntington, Surf. Sci. **116**, 522 (1982).

[14] V. V. Voronkov, Kristallografiya **12**, 831 (1967) [Sov. Phys. Crystallogr. **12**, 728 (1968)].

[15] J. M. Blakely and R. L. Schwoebel, Surf. Sci. **26**, 321 (1971).

[16] M. C. Payne, N. Roberts, R. J. Needs, M. Needels, and J. D. Joannopoulos, Surf. Sci. **211/212**, 1 (1989).

[17] A. F. Andreev and Yu. A. Kosevich, Zh. Eksp. Teor. Fiz. **81**, 1435 (1981) [Sov. Phys. JETP **54**, 761 (1981)].

[18] V. I. Marchenko and A. Y. Parshin, Zh. Eksp. Teor. Fiz. **79**, 257 (1980) [Sov. Phys. JETP **52**, 129 (1980)].

[19] See, for example, A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988), Chap. 4.

[20] T. Yamamoto and T. Izuyama, J. Phys. Soc. Jpn. **56**, 632 (1987). The original calculation of the entropic contribution to step-step repulsion appears in the appendix to E. E. Gruber and W. W. Mullins, J. Phys. Chem. Solids **28**, 875 (1967). See also C. Jayaprakash, C. Rottman, and W. F. Saam, Phys. Rev. B **30**, 6549 (1984).

[21] Suppose l_n denotes the actual length of the nth terrace of the vicinal surface and let $L=\sum_n l_n$. The cubic term in (3) then takes the form $w(a^3/L)\sum_n l_n^{-2}$, where a is the step height. This reduces to $w(h/l)^3 \equiv w\theta^3$ when all $l_n = l$. Similarly, a θ^2 contribution corresponds to an l^{-1} step-step interaction energy.

[22] See Figs. 1 and 2 in Ref. 15 for a good illustration of this.

[23] S. P. Chen, A. F. Voter, and D. J. Srolovitz, Phys. Rev. Lett. **57**, 1308 (1986).

[24] Results obtained by S. P. Chen (unpublished) for the oscillatory relaxation of Al(410) and Al(610), as quoted in D. J. Srolovitz and J. P. Hirth, Surf. Sci. **255**, 111 (1991).

[25] T. L. Einstein, CRC Crit. Rev. Solid State Mater. Sci. **1**, 261 (1978).

[26] K. H. Lau and W. Kohn, Surf. Sci. **75**, 69 (1978).

[27] D. Kalkstein and P. Soven, Surf. Sci. **26**, 85 (1971).

[28] The missing row of atoms is treated by introducing an on-site perturbation ε onto each atom in the row in question and letting $\varepsilon \to \infty$.

[29] F. Watanabe and G. Ehrlich, Phys. Rev. Lett. **62**, 1146 (1989).