Avalanche in Adhesion

John R. Smith,[(1)] Guillermo Bozzolo,[(2)] Amitava Banerjea,[(3,4)] and John Ferrante[(4)]
[(1)]*Physics Department, General Motors Research Laboratories, Warren, Michigan 48090-9055*
[(2)]*Physics Department, Case Western Reserve University, Cleveland, Ohio 44106*
[(3)]*Physics Department, Kent State University, Kent, Ohio 44242*
[(4)]*National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135*
(Received 30 May 1989)

Consider surfaces being brought into contact. It is proposed that atomic layers can collapse or avalanche together when the interfacial spacing falls below a critical distance. This causes a discontinuous drop in the adhesive binding energy. Avalanche can occur regardless of the stiffness of external supports. A simple understanding of the origin of this phenomenon is provided. A numerical calculation has been carried out for adhesion in Ni. A new wear mechanism due to avalanche is suggested.

PACS numbers: 62.20.Pn, 68.35.Md, 81.40.Pq

The energetics of adhesion has well recognized[1,2] technological significance associated, for example, with metal and semiconductor contact formation, friction,[3] wear, and crack formation.[4] Here we would like to report an avalanche effect in adhesion. Our many-atom calculations suggest that there are conditions under which solid surfaces will collapse together even when the initial interfacial spacing is significantly larger than the bulk interplanar spacing. This will happen independently of how stiffly the two solid surfaces are externally supported. Our approach allows for a simple understanding of the origins of this phenomenon. This discovery may also have significant implications for technologies involving adhesion. For example, we propose that avalanche may lead to a heretofore unrecognized wear mechanism for sliding surfaces.

Pethica and Sutton[5] first suggested that solid surfaces could jump together. They were primarily interested in a tip on flat configuration because of its relevance to the scanning tunneling microscope[6] (STM) and the atomic-force microscope[7] (AFM). Their conclusions are based on Lennard-Jones pair potential and continuum analyses, whose limitations they delineate.[5] Here we have carried out a many-atom investigation of the stability of adhering flat surfaces, and find quantitative evidence for an avalanche effect. The results suggest some qualifications on the effect for the case of STM or AFM tips, but do point the way to other technological applications such as the new wear mechanism mentioned earlier.

Let us for definiteness consider an interface between two Ni(100) crystals. We first fix the atoms in each crystal rigidly at bulk interatomic spacings and structure and compute the adhesive energies as a function of interfacial spacings. For that and subsequent calculations we use the equivalent crystal method[8,9] which is based on an exact, perturbation theory approach. This method has been demonstrated to give accurate surface energies[8] and relaxed atomic positions[9] for a number of transition-metal surfaces. The results are shown in Fig. 1, plotted as open circles. Zero separation corresponds to the bulk interplanar spacing. Note that the minimum occurs at the bulk interplanar spacing, as it should. The adhesive energy at the minimum, 3120 ergs/cm^2, is in good agreement with the Ni(100) surface energy of 3050 ergs/cm^2 as predicted from first principles.[10] One can also see that the curve is of a form similar to that found earlier for simple metals.[11]

Next, at each rigid interfacial separation we allow the atomic locations to relax to minimize the total energy. Low-index surface planes of Ni (as well as Cu, Ag, and Al) are known[9] to relax in a planar fashion, i.e., without reconstruction, which simplifies the calculation. Let us start by only relaxing the surface atomic layer on each half-space (slab), with results shown in Fig. 2. For the rigid starting separation of 2.6 Å, there is an absolute minimum for an interfacial separation d larger than 2.6 Å. This relaxation toward the bulk is typical of what is found experimentally for a variety of surfaces.[9] On the

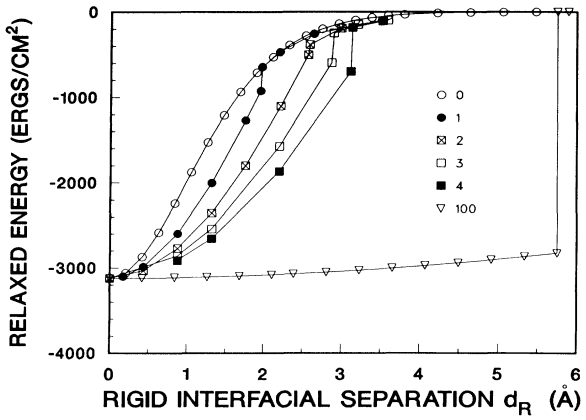

FIG. 1. Relaxed and rigid adhesive binding energies for Ni(100) crystal surfaces in registry. Rigid interfacial separation d_R refers to the separation prior to relaxation. Zero separation corresponds to the bulk interplanar spacing d_0 (see Fig. 4). The curves are numbered according to the number of surface atomic layers in each crystal that are relaxed.

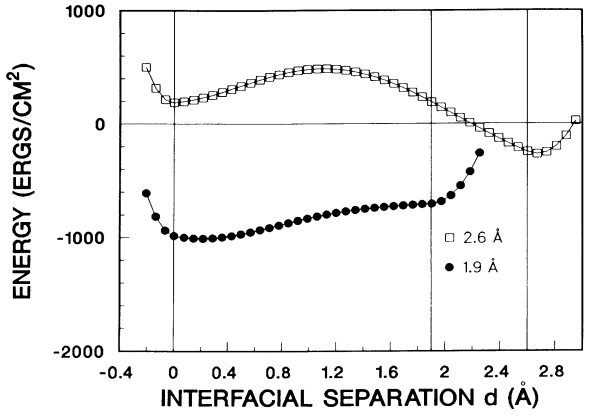

FIG. 2. Total energies as a function of symmetric movement on only the surface atomic layers of each Ni(100) crystal in a direction perpendicular to each substrate. For zero movement the interfacial spacings are 2.6 Å for the upper curve and 1.9 Å for the lower curve.

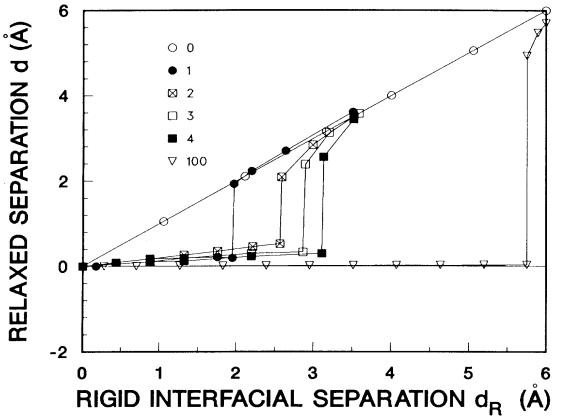

FIG. 3. Relaxed interfacial separation d as a function of rigid (unrelaxed) separation d_R between Ni(100) surfaces. The curves are enumerated corresponding to the number of surface atomic layers in each crystal that are relaxed.

other hand, Lennard-Jones pair potentials predict that surface atomic layers relax outward.[5] Note also in Fig. 2 that at 2.6 Å there is a rather large barrier which holds the surface atomic layers on their respective substrates. However, note that at 1.9 Å this barrier has disappeared, and the surface layers come together at a separation slightly larger than the bulk interplanar spacing ($d=0$ at bulk spacing). That is, when the two surfaces are pushed to within 1.9 Å of each other, the surface atomic layers cannot be held apart. This is shown also in Fig. 3 for the single- (surface) layer relaxation, where the relaxed interfacial separation is found to drop discontinuously to 0.2 Å. It is also seen in Fig. 1 by a finite drop in adhesive energy at 2 Å for single-layer relaxation. This coming together of the surface layers introduces a rather large strain, which is gradually relieved as the distance between substrates is decreased further, as seen in Fig. 1.

Now let us consider the effect of relaxing an increasing number of atomic layers. From Fig. 3 it is clear that the avalanche effect is present when the 2, 3, 4, or 100 atomic layers nearest the surface are relaxed. As the number of relaxed atomic layers N increases, one can see from Figs. 1 and 3 that the critical distance at which avalanche occurs also increases. The $N=100$ result is computed via continuum mechanics, using experimental elastic constants[12] and an applied force on each crystal equal to the gradient of the unrelaxed energy curve (open circles) of Fig. 1. Note in this case the energy drop is approximately the surface energy, i.e., of the order of 1 eV per surface atom. This is because as N increases, the strain energy decreases. This is reflected in the slopes of the energy curves of Fig. 1 after the avalanche. In the continuum limit, this strain energy decreases as $1/N$.

The critical distance is determined by a competition between an energy lowering due to surface layers from opposing surfaces being brought closer to each other and an energy increase due to surface layers being pulled away from their corresponding substrates. The energy increase is weakened as the rigid or unrelaxed separation decreases because of the spread of the electron density from the surface into the vacuum region.[13] That is, as the rigid spacing is decreased, the surface layers can move together across the interface and form bonds with each other (thereby lowering the energy), and still maintain bonds with their substrates, albeit somewhat stretched. This is because of electron wave-function overlaps connecting the substrates with the surface layers even after the latter have moved together, which in turn is due to the exponential spread of the electron density into the vacuum region from the metal surfaces. Now once the surface layers can move together, the layers beneath them can follow because wave-function overlaps between substrate and surface layers are even larger than those between surface layers separated by the original interface. For a continuum approach, as the number of relaxed layers $N\rightarrow\infty$, the critical distance $d_c\sim\ln N$. This follows immediately from the knowledge that at the separation d_c the adhesive force is equal to the restoring force and the derivatives of these two forces with respect to separation are also equal. For example, for a relaxed thickness on each Ni(100) crystal of 1.7 cm ($N\sim10^8$), $d_c=16$ Å. Thus even for relatively large thicknesses, d_c remains quite small.

The avalanche process is rapid. One can estimate the time avalanche takes from the time it takes a sound wave to travel on interplanar spacing. This is on the order of 100 fs.

Note that in some sense this avalanche process is the inverse of a fracture process. While there is hysteresis between the joining and detaching of an adhesive junction, once fracture is initiated at a given strain the junc-

tion often snaps apart. That is, the analog to a critical interfacial spacing in avalanche is a critical strain in fracture.

Avalanche does not necessarily occur. Depending on film thickness, film stiffness, and the strength of the adhesive force, the adhesive forces may be too weak relative to the restoring forces for these forces and their derivatives to ever be equal at some separation. All of these forces must be quantitatively determined in order to find whether or not avalanche will occur for any particular interface. In fact, it has generally been presumed that solid surfaces can be brought together in a continuous fashion. This perception is based on the idea that attractive forces on a surface layer from its own substrate should be larger than those from another surface because the substrate atoms are closer. We see from Fig. 2 that the perception can break down when surfaces in registry are separated by less than a critical distance. An increase in stiffness will inhibit avalanche, as shown in Figs. 1 and 3. As the number of atomic layers that are allowed to relax is decreased, the material is made effectively stiffer, and these figures show there is a corresponding decrease in the separation at which avalanche occurs. The results for the thickness effect in Figs. 1 and 3 are particularly surprising. For Ni(100) films in registry, even the stiffest films—only relaxing one atomic layer—will avalanche. Stiffness can also be incorporated through geometry. Consider an STM or AFM tip. From Figs. 1 and 3, any tip that is of the order of 10 Å or less in height will avalanche when and if the substrate avalanches. Tips that are substantially taller than that may have their own avalanche characteristics, however. For definiteness, consider a pyramidlike tip. Then the avalanche characteristics of the tip will depend on its aspect ratio, i.e., the ratio of its width to height. Generally, the higher the aspect ratio, the stiffer the tip and the more inhibited the avalanche effect. This can be understood through the competition discussed above which leads to avalanche. Consider an atomic layer somewhere in the pyramid. Suppose the layer above it is being pulled toward the other surface. The layer above it will provide a smaller adhesive force than the layer beneath it, because there are more atoms in the layer beneath it than above it. This effect is exacerbated by larger aspect ratios. As avalanche is determined by a competition between these adhesive forces, this geometrical effect will tend to inhibit avalanche.

Other factors could inhibit avalanche. For example, a lack of registry between the surfaces could lessen the adhesive forces between surface layers which must compete with forces between surface layers and their substrates. Alternatively, the large energy lowering obtainable from adhesion could be an additional driving force for distortion into registry or epitaxy. It would also be interesting to consider what role avalanching might play in crack propagation in solids. At a crack tip, surfaces are not parallel, which would tend to inhibit avalanche. However, the potential-energy gain from avalanche may tend to sharpen crack tips, i.e., to make crack tip surfaces more parallel so that the tip looks more like a cusp. Finally, a monolayer of impurities will typically[14] decrease the adhesive binding energy, and with it the propensity to avalanche.

The possibility of an avalanche suggests a new mechanism of wear. Consider two solids sliding on each other as in Fig. 4. There we show the interfaces as atomically rough over a scale of, say, 1000 Å. As the surfaces slide over each other, eventually there will be regions which are in registry and for which the interfacial spacing becomes less than the critical spacing. Then an avalanche could occur, joining together regions which otherwise would not have been joined. After the avalanche, a single-crystal junction has been formed across the interface. As the sliding continues, this avalanched junction would necessarily be cracked apart. Because of the avalanche, there is a hysterisis in total energy versus interfacial spacing. That is, the newly formed crystalline junction will not necessarily crack at the original interface and so wear particles can be formed. Thus this fracturing of the interface is a wear mechanism that would not have happened without avalanche. One can envision avalanches occurring and junctions being cracked open over and over again as the sliding proceeds.

In summary, we have carried out many-atom calculations of Ni(100) adhesion. We find that an adhesive avalanche can occur in which the atomic layers fall together across the interfacial gap between solid surfaces, independent of the strength of external supports. This causes a discontinuity in the total energy as large as of the order 1 eV per surface atom when the separation falls below a critical distance of the order of angstroms. The avalanche process takes of the order 100 fs. A dependence of film thickness was found. As the Ni(100) film thickness increases, the stiffness decreases so that

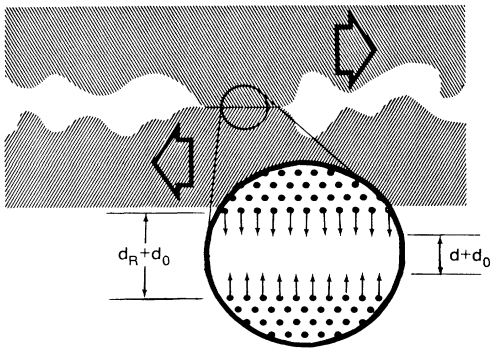

FIG. 4. Cross section of sliding surfaces. Inset: Region which has avalanched together, with arrows showing the displacements of the atoms in the surface layers due to avalanche. Also shown are the rigid interfacial separation d_R+d_0 and the relaxed interfacial separation $d+d_0$, where d_0 is the bulk interplanar spacing.

the critical separation at which avalanche occurs increases. This tendency to avalanche can be understood as a competition between adhesive energies between surface layers across the interface and between surface layers and their corresponding substrates. It is most likely to happen for planar interfaces in commensuration. Lack of registry (commensuration) across the interface and surface impurity layers may prohibit avalanche or decrease the separation at which it occurs, depending on film stiffness.

A new wear mechanism was proposed which involves avalanche. That is, when high points on the surfaces are slid into commensuration and have interfacial separation below the critical distance, they will avalanche together. This junction will then have to be cracked open as the sliding continues, yielding wear particles.

The authors would like to thank Charles Olk for useful discussions.

[1]N. Martensson, A. Stenborg, O. Bjorneholm, A. Nilsson, and J. N. Andersen, Phys. Rev. Lett. **60**, 1731 (1988).

[2]*Panel Report on Interfacial Bonding and Adhesion,* edited by John R. Smith [Mater. Sci. Eng. **83**, 169–237 (1986)].

[3]C. Mathew Mate, Gary M. McClelland, Rangnar Erlandsson, and Shirley Chiang, Phys. Rev. Lett. **59**, 1942 (1987).

[4]S. C. Langford, D. L. Doering, and J. T. Dickinson, Phys. Rev. Lett. **59**, 2795 (1987).

[5]J. B. Pethica and A. P. Sutton, J. Vac. Sci. Technol. A **6**, 2494 (1988).

[6]G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).

[7]G. Binnig, C. F. Quate, and Ch. Gerber, Phys. Rev. Lett. **56**, 930 (1986).

[8]John R. Smith and Amitava Banerjea, Phys. Rev. Lett. **59**, 2451 (1987).

[9]John R. Smith and Amitava Banerjea, Phys. Rev. B **37**, 10411 (1988). For discussion of rigid adhesion energetics, see Amitava Banerjea, John Ferrante, and John R. Smith, MRS Symposia Proceedings, Boston, 1989 (Materials Research Society, Pittsburgh, to be published).

[10]John R. Smith, John Ferrante, Pascal Vinet, J. G. Gay, Roy Richter, and J. H. Rose, in *Chemistry and Physics of Fracture,* edited by R. H. Jones and R. M. Latanision (Martinus Nijhoff, Hingham, MA, 1987), p. 329.

[11]John Ferrante and John R. Smith, Phys. Rev. B **31**, 3427 (1985); Amitava Banerjea and John R. Smith, Phys. Rev. B **37**, 6632 (1988).

[12]Charles Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1956), 2nd ed., p. 93.

[13]John R. Smith, Jack G. Gay, and Frank J. Arlinghaus, Phys. Rev. B **21**, 2201 (1980). For Ni(100) results, see X. Zhu, J. Hermanson, F. J. Arlinghaus, J. G. Gay, R. Richter, and J. R. Smith, Phys. Rev. B **29**, 4426 (1984).

[14]John R. Smith and T. Vincent Cianciolo, Surf. Sci. **210**, L229 (1989).