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Adhesion between atomically flat metallic surfaces

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The study of adhesive interactions between atomically flat surfaces in close proximity requires that their separation be controlled and known to within a tenth of an angstrom. In some instances, however, two solids will display a structural instability of their surface layers as their separation approaches the bulk value. When this occurs, an abrupt transition, termed "adhesive avalanche," from a geometry with two spatially distinct surfaces to a single homogeneous structure takes place as the surfaces are brought to within 1–2 Å of their equilibrium bulk separation. The avalanche event is the result of a critical growth in the adhesive force gradient at each surface as their separation is reduced to a critical value. We have applied the embedded-atom method to examine this phenomenon for (001)- and (111)-oriented Ni, Cu, and Au surfaces. Both statics and dynamics of adhesion are considered, revealing that tensile stress waves are generated upon avalanche and eventually decay into heat due to the effects of dispersion and dissipation. These tensile waves are associated with a wavelike transmission of the adhesive force, caused by the occurrence of the avalanche event. The presence of avalanche events will cause difficulties in the interpretation of experimental studies of interfacial forces.

I. INTRODUCTION

Adhesion forms the very basis of materials science where, in the absence of adhesive binding, there would be few materials useful for technological applications. As a result, the study of adhesion has been of great concern from the earliest days of modern science, when various mechanical mechanisms describing adhesion (e.g., Velcro-like "atoms") (Ref. 1) were proposed. When thermodynamics became established, however, it was clear that adhesion between materials resulted from the recovery of surface energy of separated bodies during the process of establishing surface contact. Thus, the thermodynamic energy of adhesion is defined as the sum of energies of the isolated surfaces minus the energy of the interface resulting from adhesion, that is,

$$E_{\text{ad}} = E_{\text{surface}} - E_{\text{interface}} . \tag{1}$$

Quantum mechanics now allows us to understand, at least qualitatively, the source of surface energy (e.g., reduced coordination at surfaces, dangling bonds in covalent materials, etc.). We may also, in particularly simple cases, describe the process of recovery of the surface energy via formation of adhesive interactions for simple, clean, atomically flat adhering surfaces. Current theoretical treatments, however, are inadequate to treat adhesion between structurally or chemically nonideal surfaces of complex materials. As a result, both careful experimentation and atomistic models can play crucial roles in the study of adhesion in realistic circumstances.

Adhesion typically involves the process of the formation of a buried interface and is therefore difficult to investigate experimentally. The most common techniques used to study adhesion are crude engineering tests (e.g., peel and friction tests) (Ref. 2) designed to yield statistical failure data for practical materials. Unfortunately, such tests provide little or no information on the fundamental physics and/or chemistry underlying the phenomenon of adhesion.

Even the thermodynamic evaluation of total adhesive energy is an exceedingly difficult problem. Both the surface and interfacial energies must be measured, quantities which are difficult to obtain experimentally. Given that such measurements are successfully carried out, however, these experiments still give no information on the *process* of recovery of the surface energy. As the surfaces approach, the surface states change adiabatically with separation (primarily in the last few angstroms), evolving into a final interfacial state. Current experimental techniques provide little insight into this evolution of surface states during surface approach and contact. As such changes are at the heart of the adhesive process, the absence of experimental information on these changes represents a serious impediment toward understanding the *formation* of the adhesive interactions.

II. EXPERIMENTAL MEASUREMENT OF INTERFACIAL FORCES

Adhesive interactions between two materials develop when their surfaces are brought close enough together (generally less than a few angstroms separation) to cause significant overlap of electronic surface states. Following the detailed evolution of all relevant surface states during the development of adhesive interactions is generally beyond current abilities. However, experimental techniques can provide direct measurement of the interfacial forces between two bodies whose surfaces are maintained at constant subnanometer spacings. Such measurements should, in principle, determine the dependence of adhesive energy on spatial separation. Although this is an "averaged" quantity, in that the evolution of particular surface and interfacial states is not traced, the information should provide a useful comparison with more comprehensive models of the interfacial interactions.

Such experiments require the development of apparatus having extraordinary sensitivity and precision. The interfacial separation must be both controlled and measured to within approximately 0.1 Å to be useful in following the complex adhesive interactions. Several considerations, including the ability to control the angle between two surfaces and the desire to examine surface regions that are free of unintentional defects (e.g., surface steps), limit the physical dimensions of such an experiment. One is thus faced with the need to position a 100-Å tip-diameter probe several angstroms above the sample surface with a separation distance controlled to within 0.1 Å and a surface misalignment less than 1 mrad.

Similar challenges are encountered in atomic force microscopy (AFM).[3] AFM is a technique which has proven to have considerable potential as a qualitative surface imaging tool with subangstrom resolution. In its basic form, AFM involves moving an atomic-size tip over the surface of a sample. This allows measurement of a constant force contour reflecting the "shape," in some sense, of surface features. The advantage of AFM over related techniques, such as scanning tunneling microscopy, is that the tip and sample need not be conductors, thereby permitting a wider range of applications.

This early success has driven considerable interest in developing AFM into a *quantitative* tool for study and analysis of surface and interfacial energetics. Perhaps the simplest application of such a probe would involve measuring the interfacial force between a sample surface and tip as a function of separation. Integration of the force from infinite separation would, in principle, allow the adhesive energy to be determined as a function of the tip-mount–sample-mount separation. Despite obvious difficulties in the preparation of appropriate apparatus, considerable strides toward this goal have recently been made.

Several groups[4–7] are currently conducting experiments on adhesive phenomena in a range of materials using force microscopy and related techniques. As there is little previous data or theoretical understanding to guide these efforts, a substantial role exists for atomic-scale simulation of the development of adhesion between solids. Atomic-scale simulation, which depends on simplified descriptions of atomic interactions, is quite appropriate in the study of adhesion. Systems consisting of thousands of atoms can be studied, and the primary output of the simulation is the energy and physical structure of a relaxed system, or the phase-space trajectory of a dynamic system. This approach is employed in the present theoretical study of adhesion.

III. SIMULATION OF ADHESION BETWEEN ATOMICALLY FLAT SURFACES

Our objective in this study is the investigation of adhesive phenomena in monatomic metals via atomic-scale simulation. Nickel, copper, and gold were chosen for this initial study because their structural energetics are reasonably well treated using the embedded-atom method (EAM) developed by Daw and Baskes.[8] The EAM is a many-body classical treatment of the total energy of a system of interacting atoms. In addition to a pairwise interaction between ions, each atom has an embedding energy associated with the local magnitude of the electron density, thereby giving rise to many-body contributions. The resulting model is loosely based on density-functional theory, but relies on such extreme approximations that it applies directly only to a rather small class of materials. In such materials, however, enough of the bonding physics is retained that the resulting description is remarkably accurate over a wide range of problems, including surfaces, interfaces, and defects, both point and linear. The EAM is therefore the appropriate interatomic model for the present study. In particular, the fit developed by Foiles, Baskes, and Daw for a series of six fcc metals[9] including Ni, Cu, and Au is employed.

In this initial study, we chose to investigate the interaction of a pair of planar surfaces. This permits us to examine the elementary phenomena associated with adhesion without worrying about the effects of more complex geometries. The particular geometry used in this study appears schematically in Fig. 1. The similarity to atomic force microscopy is obvious, and for convenience, we adopt the terminology of "sample" and "tip" to denote the lower and upper structures, respectively. The sample and tip have the same crystallographic orientation, that is, either (001) or (111), and are initially in structural registry, so that the atomic planes line up properly. We studied only systems in which the tip and sample were composed of the same material, which allowed the interfacial energy to be ignored. Each body possesses 30 or 32 atoms on its surface plane [for the (111) and (001) orientations, respectively], and possesses periodic boundary conditions on the lateral boundaries, so that the model simulates a pair of infinite, parallel surfaces in close proximity.

Both the tip and sample structures possess three nondeformable (fixed) atomic planes which double as rigid mounts and are actually manipulated during the simula-

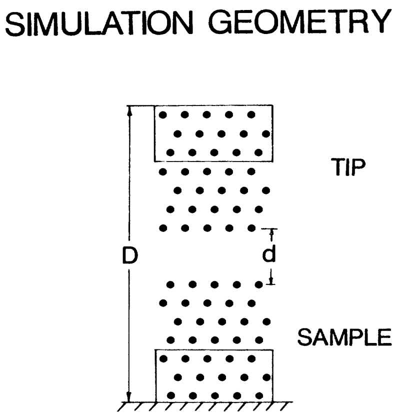

FIG. 1. Simulation geometry of interacting tip and sample structures. *D* denotes the rigid mount separation and *d* is the interfacial separation beyond bulk interplanar spacing.

tion. (Three fixed planes are sufficient to provide an extended bulklike environment for the moving planes.) The deformable portions of the tip and sample are each represented by four planes of atoms which are free to move and deform in response to interatomic forces. The total height, consisting of rigid and deformable sections for both tip and sample, was chosen as a reasonable compromise between simulating a bulklike environment and overloading our computational resources.

In order to accurately describe the process of adhesion between two solids, we need to define several physical quantities. Separation control between the tip and sample structures is performed by varying the distance between their respective groups of rigid planes. Thus, we define the rigid mount separation D as the distance between the outermost fixed planes of the two bodies (see Fig. 1). Another length scale of importance is the separation between the interacting surfaces. This is referred to as the interfacial separation d, which is defined as the distance (beyond bulk separation) between the two outermost surface planes of the respective bodies (see Fig. 1). In practice, we subtract off a constant (specifically, the sum of the initial lengths of the tip and sample structures) from the rigid mount separation D so that $D=d$, when the bodies are initially positioned. Finally, the binding energy E of the two bodies at a given separation D is obtained by subtracting the structural energy of the system with surfaces at infinite separation from the structural energy corresponding to the specified separation.

In our study of adhesion, the tip and sample structures are initially placed so that the surfaces experience essentially no interaction with the adjacent structure. This is accomplished by setting the rigid mount separation D so that the interfacial spacing d, prior to relaxation of the surfaces, is 2.5 Å. This initial condition was found to be adequate for all studies reported herein. Molecular-dynamics techniques are used to determine the structural response of the complete system. Specifically, the forces exerted on the mobile atoms are calculated based on the interactions with their surrounding atoms, and the corresponding accelerations integrated to obtain the atomic motions. A viscous drag term is imposed on the atomic motions to dampen out transient oscillations and maintain a thermal energy near zero.

The metal systems considered in the present study display inward surface relaxations ranging from 0.01 Å for Ni(001) to 0.13 Å for Au(001). To simulate adhesive phenomena between these materials properly, we account for the possibility of surface relaxation prior to the adhesion process. Accordingly, the first step of the simulation is to relax the surfaces of both bodies. This is accomplished by maintaining the initial rigid mount separation D at a sufficiently large distance such that surface interactions are nonexistent while proceeding with the molecular-dynamics procedure. Once the system has reached equilibrium, the simulation of adhesion is started. The two rigid mounts approach each other at a constant rate of 0.1 Å/ps. This rate was chosen as a compromise permitting the simulation to conduct a continuous approach and retreat motion between the tip and sample rigid mounts while not exceeding our computational resources. The motion of the rigid mounts is continued until a minimum in the binding energy is encountered. The mounts are then moved apart, again at 0.1 Å/ps, to provide a cyclic history of the adhesion process up to the point of separation via fracture. This procedure allows us to track the detailed physical state of the system, including interfacial separation, binding energy, and adhesive force, as a function of rigid mount separation.

Figures 2 and 3 display the interfacial separation d and binding energy E as a function of rigid mount separation as the tip and sample are brought together. The primary result is that adhesive avalanche is observed in all systems studied. First predicted by Pethica and Sutton,[10] an adhesive avalanche is a sudden decrease in the interfacial separation between the tip and sample surfaces, along with a precipitous drop in binding energy, as the surfaces are brought together. The occurrence of an adhesive avalanche reflects an abrupt transition from an initial system consisting of two distinct structures with separate surfaces to a strained, single body with no identifiable surfaces remaining. A detailed discussion of this phenomenon appears later in Sec. IV. Oscillations in d and E, shown in Figs. 2 and 3, are the result of avalanche-induced wave motion propagating back and forth in the newly formed structure between the rigid mounts. (The oscillations decay due to the viscous dampening imposed on the atomic motions.) The nature of this wave motion is discussed further in Sec. VI. Denoting the value of the interfacial separation at which the avalanche occurs as d_A, we find that $1.4 < d_A < 2.2$ Å in all three materials and both orientations. These values for d_A, however, differ from those obtained for Ni(001) by Smith *et al.*[11] whose values are 60–80 % greater than those presented here. These differences result from the use of different models for atomic interactions. Although the model employed by Smith *et al.* incorporates similar length scales for these interactions, it yields surface energy values that are 50–130 % greater than those calculated by the EAM.[9] (EAM surface energy values can be determined from Figs. 3 by halving the binding energy value corresponding to zero separation, i.e., for $D=0$). Results of the present study show that for each material, as the surface energy increases, so does the interfacial separation at which the adhesive avalanche occurs.

The effect of intrinsic surface relaxations on the avalanche process was examined by simulating the adhesion process between Au surfaces. Little distinction appeared between the Au results and those for Ni and Cu, despite the large surface relaxation exhibited by Au. In fact, the only significant effect appears to be a reduction in the interfacial separation d_A, at the onset of avalanche, by an amount roughly equivalent to the initial, relatively large, inward surface relaxation of between 0.1 and 0.2 Å.

Since experimental studies of adhesion can typically provide data on retreat (i.e., separation) as well as approach, we have also simulated a complete approach-retreat cycle for the Cu(111) system. The results of this simulation are shown in Figs. 4(a) and 4(b) displaying the binding energy and adhesive force, respectively, as functions of rigid mount separation D. On the approach leg

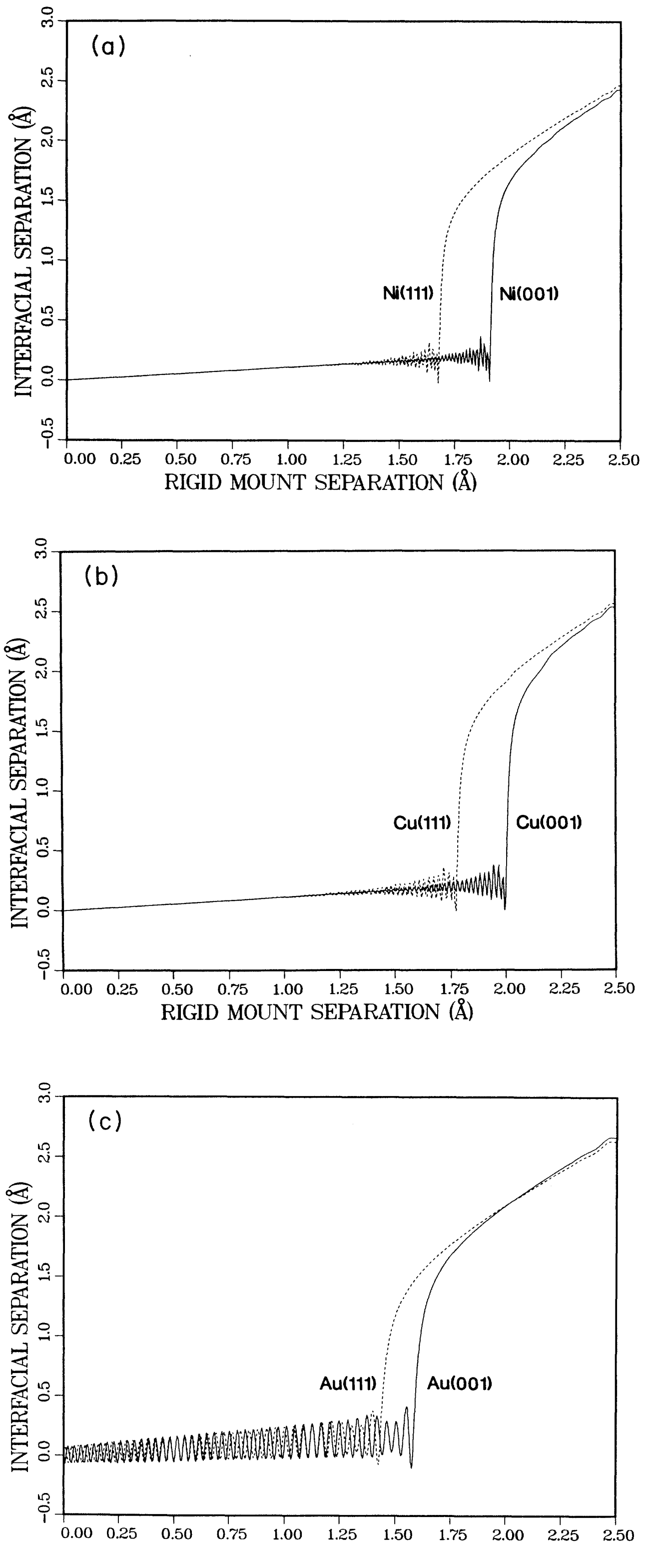

FIG. 2. Interfacial separation d as a function of rigid mount separation D for (001) and (111) surfaces: (a) nickel, (b) copper, and (c) gold. Abscissa values denote the rigid mount separation minus the initial lengths of tip and sample structures. Bulk interplanar spacing corresponds to $D,d=0$.

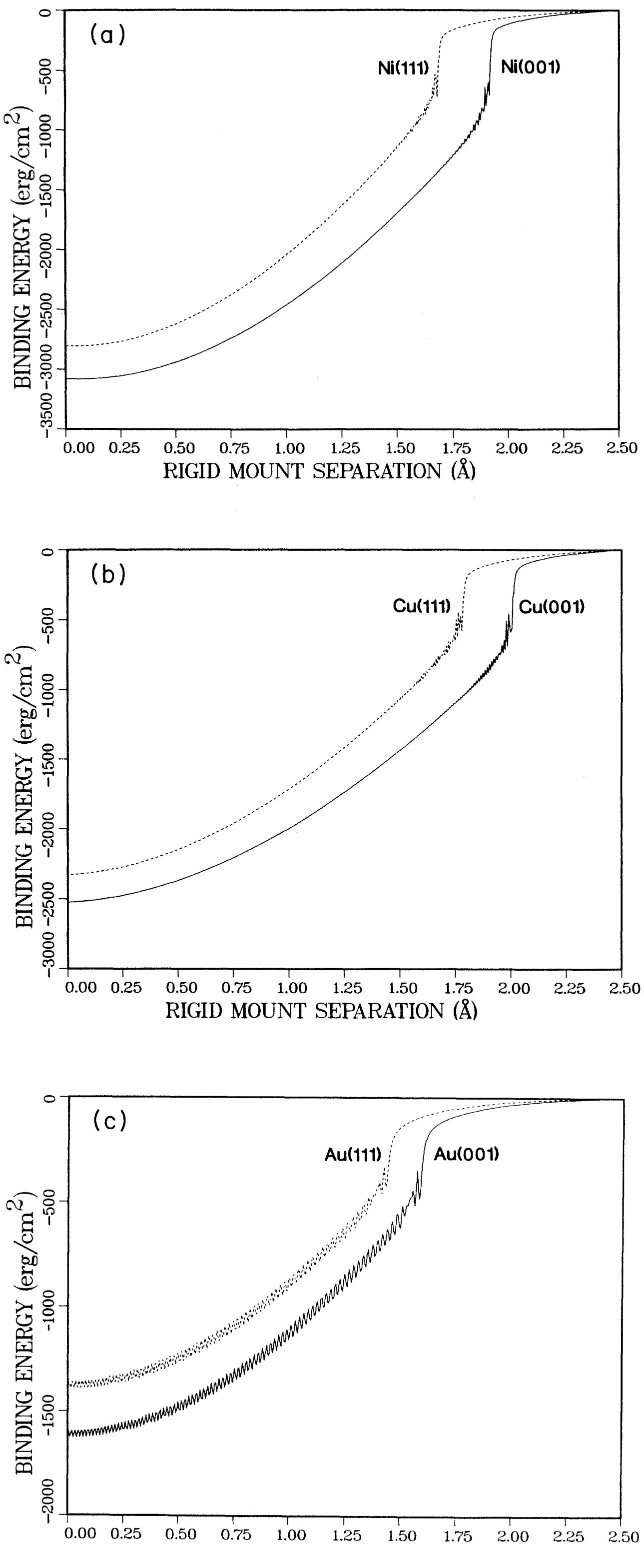

FIG. 3. Relaxed binding energy E as a function of rigid mount separation D for (001) and (111) surfaces: (a) nickel, (b) copper, and (c) gold. At bulk interplanar spacing ($D=0$), the E values correspond to twice the surface energy.

of the plots, as the rigid mount separation is decreased from its initial value of 2.5 Å, an adhesive avalanche at $D=1.8$ Å causes the energy to drop precipitously and the adhesive force to display a spike profile. At this point, the force displays a 40-fold increase of its preavalanche value and then quickly decays to a nominal value on a new curve, all within a time period of between 1–2 ps. As D is decreased further, both the energy and force plots follow paths that are distinctly different from those corresponding to the preavalanche behavior. The postavalanche ($D < 1.7$ Å) response of the system reflects an elastic behavior of the newly formed structure as indicated by the fairly precise overlay of the retreat leg, in which D is increased from the zero-strain state (at $D=0$) to structural failure. In fact, the retreat leg reflects elastic behavior of the single structure practically up to a brittle-like failure at $D \sim 3.3$ Å (roughly 20% tensile strain). This type of behavior is typical of the tensile response of defect-free, single-crystal solids.[12]

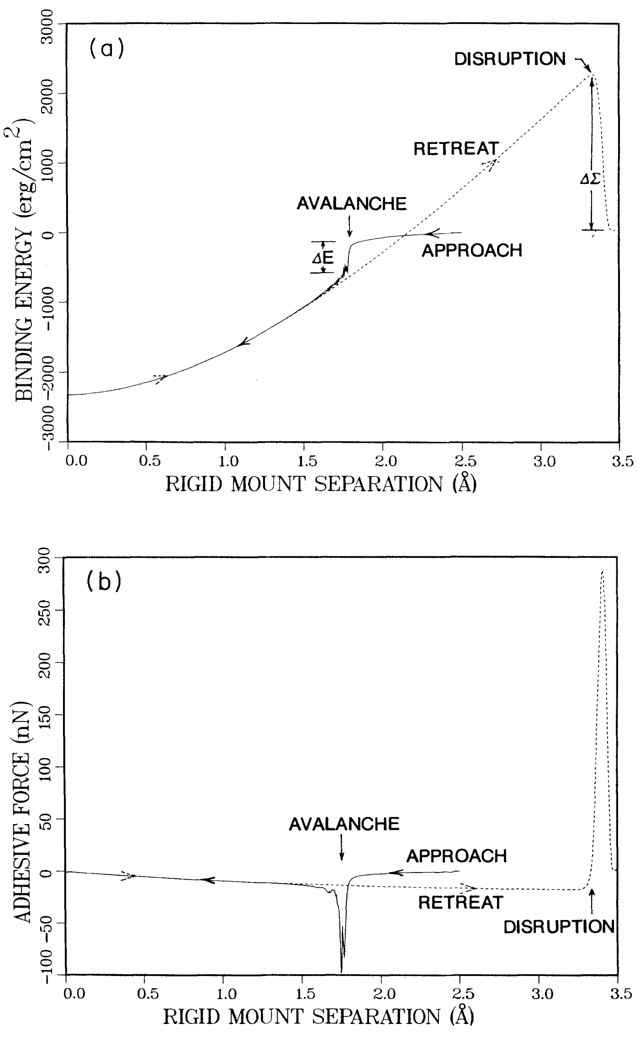

FIG. 4. (a) Binding energy and (b) adhesive force as functions of rigid mount separation D for Cu(111) when subjected to a complete approach-retreat cycle. ΔE and $\Delta\Sigma$ denote the abrupt changes in binding energy while the system undergoes adhesive avalanche (during approach) and tensile disruption (during retreat), respectively.

The influence of size effects was investigated by conducting a simulation employing a Cu(111) model with tip and sample structures each consisting of 16 moving planes (a fourfold increase over the smaller model) and three rigid planes (acting as rigid mounts). The results of this simulation are qualitatively identical to those reported above. The only significant quantitative difference is in the value of rigid mount and/or interfacial separation at which adhesive avalanche occurs. Specifically, this model displays avalanche at $D=2.12$ Å, in contrast to our smaller model which undergoes avalanche at $D=1.77$ Å. This result is not surprising since the larger model will have a smaller effective "spring constant" due to its increased length and, hence, avalanche at a reduced value of adhesive force which would be developed earlier in the approach, that is, at a greater separation.

IV. ADHESIVE AVALANCHE

Adhesion across an interface will be referred to here as "strong" if, as the surfaces approach one another, the adhesion process between them includes the occurrence of an adhesive avalanche. The interpretation of interfacial force experiments can be difficult when systems exhibiting strong adhesion are studied. This is due to the fact that the force-distance relation can only be integrated down to the avalanche threshold to provide adhesive energies. Below that value, the interfacial force results from elastic interactions in a strained single material, rather than from adhesion between distinct material surfaces. At this time, it is not known how common strong adhesion is. However, adhesive avalanche phenomena have been identified in simulations of several clean metallic systems, as described above, and between clean and properly oriented Si(111) surfaces.[13]

In adhesive avalanche, the interfacial separation d changes discontinuously from the preavalanche value d_A to the post avalanche value d_P. (d_P is usually close to zero, and is expected to be so in macroscopic systems.) The quantity which is actually controlled during an experiment is the rigid mount separation D. When the interfacial separation d is large enough such that there exists no significant adhesive interactions, there will be a simple linear relation between d and D. As the adhesive forces between the two surfaces begin to grow, however, the tip and sample will respond elastically to those forces. When this occurs, the simple linear relation between d and D is broken. At the onset of adhesive avalanche, a small change in D from D_A $[=D(d_A)]$ to $D_A-\epsilon$ $(\epsilon \ll 1)$ will result in a large change in the interfacial separation (d_A to d_P) over a time period of a few picoseconds. Current experimental techniques are not sensitive on such short timescales and thus, this region will be inaccessible to force measurement.

The results in Fig. 4 suggest the dependence of binding energy E on d as shown in Fig. 5 for particular values of D. When the surfaces are well separated [Fig. 5(a)], the E-vs-d curve has only a single minimum, corresponding

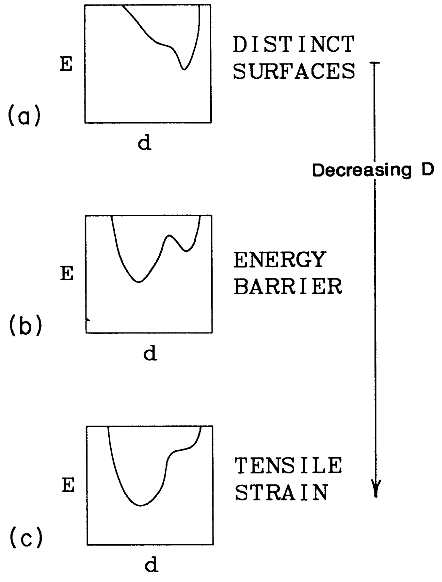

FIG. 5. Schematic illustration of the dependence of binding energy E on the interfacial separation d for various values of rigid mount separation D: (a) large separation, no surface interaction; (b) preavalanche, surfaces interacting; (c) postavalanche, surfaces eliminated.

to totally relaxed surface layers on both tip and sample. As the bodies approach, a point is reached where the surfaces attract each other [Fig. 5(b)], resulting in a nonlinear dependence of d on D. At the relative position shown here, the postavalanche state (smaller value of d) is energetically favorable, but requires activation over a large energy barrier. At the point of avalanche ($D = D_A$), the energy barrier vanishes. The result [Fig. 5(c)] is an abrupt transition from a system consisting of two distinct structures with surfaces separated by roughly 2 Å (beyond bulk separation) to a single, strained structure. Beyond this point, reduction of D leaves d essentially unchanged as the unstrained bulk state is reached. The essential feature of the adhesive avalanche is the disappearance of the energy barrier separating the small-d state from the large-d state. This event, which is the hallmark of strong adhesion, produces a singular force on the surface atoms, driving an abrupt reduction in interfacial separation.

V. INTERPRETATION OF INTERFACIAL FORCE MEASUREMENTS

Adhesive interactions may be studied via AFM techniques by measuring the force F between surfaces at varying tip-mount–sample-mount separations D. In principle, then, the F-vs-D relation could be integrated inward from infinite separation, yielding the binding energy E as a function of D. If the surface energies are known independently (perhaps through interfacial force measurements on each material separately), the interface energy could then be extracted from such measurements. However, interfacial force measurements will be difficult to interpret when adhesive avalanches occur. In this case, the dependence of d on D is discontinuous (or very nearly so). The problem here is that avalanche does not occur when the energies of the preavalanche and postavalanche states are equal. The present simulations and the earlier work of Smith *et al.* agree that there is a substantial energy barrier to overcome when these two states are of equal energy. Avalanche occurs only when this energy barrier disappears. The preavalanche and postavalanche energies then differ by a value ΔE [see Fig. 4(a)], referred to here as the avalanche energy, with the postavalanche state having the lower energy. This effect was schematically illustrated in Fig. 5, where the energy barrier (E vs d) is plotted as a function of D. The avalanche energy ΔE is related to the adhesive energy E_{ad} through

$$\Delta E = E_{\mathrm{ad}} - E_A^S \,, \tag{2}$$

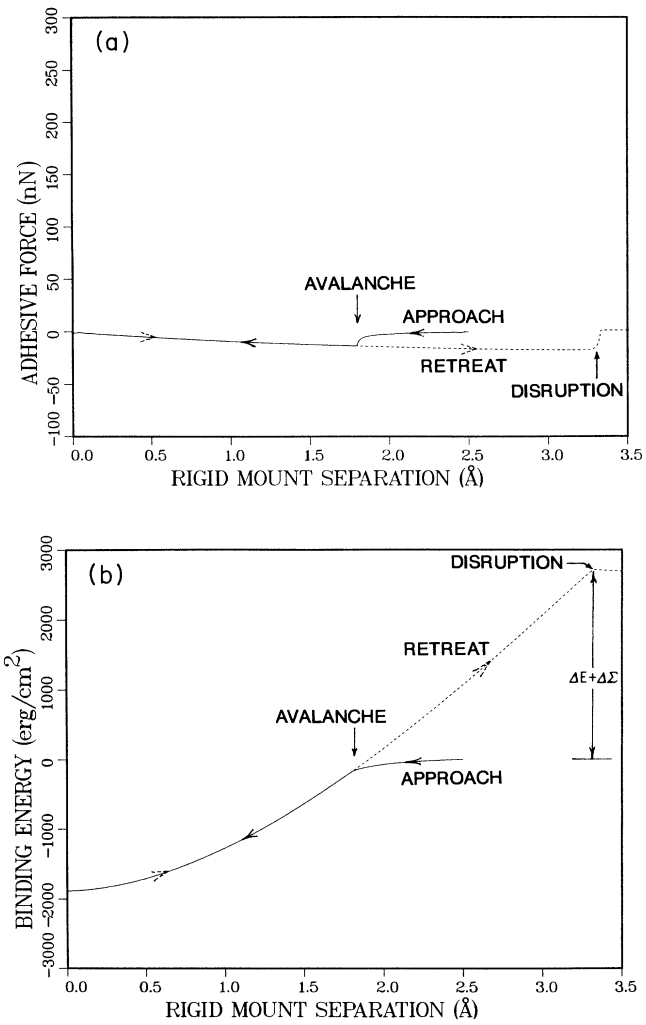

FIG. 6. (a) Predicted AFM measurement of adhesive force F as a function of rigid mount separation D for Cu(111). (b) Binding energy E as a function of D determined by integration of adhesive force data plotted in (a). See Fig. 4 caption for the definitions of ΔE and $\Delta \Sigma$.

where E_A^S is the strain energy of the newly formed structure at the strain imposed just after avalanche, i.e., at $D=D_A$. [Recall the definition of E_{ad} as described by Eq. (1)].

Unfortunately, without the ability to measure adhesive forces on picosecond timescales, an experimentally determined F-vs-D plot for a strongly interacting system undergoing avalanche would appear similar to the one in Fig. 6(a). In this case, the force spike associated with the avalanche event would not be present. Then, when integrated, this plot would necessarily lead to a binding energy E-vs-D plot [Fig. 6(b)] that neglects the drop in energy associated with the event, that is, the avalanche energy would be overlooked. As further discussed in Sec. VI, this omission will lead to incorrect conclusions whenever one attempts to use these results to determine the energy associated with the adhesion process. The predicted adhesive force spike [in Fig. 4(b)] is attractive in nature, causing the tip to abruptly move toward and impact with the sample surface, thereby generating wave motion on picosecond timescales.

VI. AVALANCHE-DRIVEN STRESS WAVES

As we have shown thus far, the occurrence of an avalanche event is associated with abrupt decreases in the binding energy and interfacial separation. Furthermore, our results show that as the rigid mount separation is decreased to the point of incipient avalanche, a critical buildup occurs in the adhesive force gradient. Consequently, at the onset of avalanche, the outermost surface planes abruptly move toward the interface, thereby transmitting the adhesive force onto the second-level atomic planes which, in turn, move in response towards the interface, and so on. The result is a wavelike transmission of the adhesive force and the formation of a tensile wave which propagates back into each bulk structure, away from the interface. In the materials examined here, the adhesive forces developed during the avalanche produce atomic velocities of several hundred m/s at the surfaces for a duration of about 0.5 ps. We have examined this phenomenon[14] during avalanche between Cu(001) surfaces. This dynamic simulation was carried out using a conventional molecular-dynamics technique and the EAM treatment of atomic interactions. An infinite plate about 100 Å thick was allowed to adhere to a fixed Cu wall. The avalanche generated a strong (~ 10 GPa) tensile wave of picosecond duration into the plate. As the tensile wave propagated through the material, dispersion and scattering converted the stress energy of the wave into heat. Lattice vibrations were generated at the interfacial region from the atomic motions set up there as a result of the avalanche event. Eventually, the entire avalanche energy ΔE was converted into heat.

The occurrence of an adhesive avalanche poses difficulties in the measurement of adhesive energy by means of AFM-type techniques. On approach, the adhesive energy would be considered to be the difference in binding energies of the initially separated state and the final minimum-energy bulk state. With the occurrence of an avalanche, a fraction of this energy difference, i.e., a fraction of the adhesion energy, would consist of the avalanche energy ΔE. As we have mentioned, the avalanche energy is irreversible, leading to wave motion and eventual heating. Since this energy would not be determinable through atomic force measurements (due to the inability to detect the adhesive force spike at avalanche), any experimental analysis would arrive at an incorrect value for the adhesive energy. In fact, our results suggest that the inability to measure the adhesive forces during avalanche will lead to an incorrect determination of the adhesive energy by at least 20% relative to the correct value.

VII. TENSILE DISRUPTION IN STRONGLY ADHERING SYSTEMS

The process of disruption of a single material, that is, tension-induced fracture resulting in two bodies possessing distinct, fairly smooth surfaces, proceeds in a fashion similar to that of adhesion. In a sense, it is necessary to "overstretch" the material to eliminate the energy barriers against damage nucleation and surface formation. This means that an excess elastic energy $\Delta\Sigma$ is released at the abrupt formation of new surfaces [see Fig. 4(a)]. (We tacitly assume that disruption occurs on a well-defined plane, with no concommitant damage.) The excess elastic energy $\Delta\Sigma$ is related to the adhesive energy E_{ad} through

$$\Delta\Sigma=E_D^S-E_{\text{ad}} , \tag{3}$$

where E_D^S is the strain energy of the system at disruption. As distinct surfaces are formed, compressive waves and surface excitations fueled by the excess energy $\Delta\Sigma$ are generated. This is a general behavior, in contrast to that of adhesive avalanche.

The abrupt release of the excess elastic energy $\Delta\Sigma$ at disruption confuses the identification of adhesive energy in a manner similar to that due to the energy release during adhesive avalanche. That is, in a laboratory experiment, the adhesive energy would be considered to be the amount of energy necessary to separate the structure at the interface and form two surfaces. Referring to Fig. 4(a), we see that this would, in fact, be the strain energy of the system at disruption. From Eq. (3), we see that the energy then *perceived* to be the adhesive energy (which is, in fact, E_D^S) would, in reality, be the true adhesive energy E_{ad} plus the excess elastic energy $\Delta\Sigma$. Furthermore, due to the lack of experimental resolution on picosecond timescales, the adhesive forces during both adhesive avalanche and tensile disruption would not be measurable. That is, instead of measuring the adhesive forces between Cu(111) surfaces as shown in Fig. 4(b), experimental techniques would yield data similar to that illustrated in Fig. 6(a) which omit force data during avalanche and disruption. Thus, a determination of energies via an integration of adhesive force data from a complete cycle consisting of approach, adhesion (including avalanche), retreat, and disruption, would necessarily omit both the avalanche and excess elastic energies ΔE and $\Delta\Sigma$. This result is illustrated in Fig. 6(b) where it becomes obvious that by using the zero-strain state binding energy value (at $D=0$) determined from the approach data as a starting point for the retreat leg, the strain energy value at disruption will then include both ΔE and $\Delta\Sigma$. That is, the experimentally determined adhesive energy, determined using adhesive force data along the retreat leg, will now differ from its correct value by the amount $\Delta E + \Delta\Sigma$. In principle, then, the sum of the two dynamic energies ΔE and $\Delta\Sigma$ can be determined by complete-cycle adhesion experiments. Presently, however, there does not seem to be any experimental technique or analysis which allows these energies to be determined separately. For the Cu(111) system considered here, as taken from Fig. 4(a), $E_{\mathrm{ad}} = 2330$, $\Delta E = 520$, and $\Delta\Sigma = 2235$ erg/cm^2. Hence, an experimental determination of the adhesive energy would lead to a value of 5085 erg/cm^2, which exceeds the true value by roughly 120%. Even if adhesive avalanche is not present during approach, the error in assuming that the energy of separation is equal to the adhesive energy will be on the order of 90–100 % greater than the correct value.

These values represent a worst-case scenario, since we have started with perfectly smooth surfaces initially in registry, which when brought together, form a defect-free interface. Consequently, during retreat, we are faced with subjecting a perfect crystal structure to tensile strain rather than one containing a distinct interface consisting of various defects and/or faults. Hence, to achieve disruption of this structure, it is necessary to provide the additional energy to overcome the barrier against damage nucleation. If instead, for some reason, the interface had formed in a defective state (e.g., due to out-of-registry or misalignment), the energy necessary for disruption would be substantially reduced due to stress intensification at the site of the interface. However, with the ability of AFM-type experimental techniques to resolve surface features on an atomic scale, we are in a position to characterize and study near-perfect as well as defective surfaces in order to provide a clearer understanding of the adhesive process between different types of surface structures. With this ability at hand, it seems prudent to investigate the more perfect structures first, so that the influence of defects and faults on the adhesion process can then be isolated and understood in turn.

VIII. SUMMARY

We have performed atomic-scale studies of the adhesion process between two metallic surfaces. These studies have revealed the occurrence of an abrupt structural transition taking place at small separations between the surfaces due to an avalanche in the adhesive forces between them. This adhesive avalanche is associated with large adhesive forces of picosecond duration and the formation of tensile stress waves due to the wavelike transmission of the adhesive forces away from the interface. Separation of the newly formed structure up to disruption (i.e., fracture) requires the input of additional energy to overcome the energy barriers against nucleation of damage and surface formation. Disruption occurs in a manner somewhat similar to that of an adhesive avalanche, that is, a significant amount of the strain energy (roughly 50% in this case) is released, causing compressive waves to form and propagate away from the newly formed surfaces. Such overall behavior makes the determination of adhesive and interfacial energetics from experimentally acquired adhesive force data difficult to perform with strongly adhesive materials.

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