

GAS-SURFACE REACTIONS: MOLECULAR DYNAMICS SIMULATIONS OF REAL SYSTEMS*

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* We would like to dedicate this chapter to Don E. Harrison, Jr., a dear friend and colleague, who died during the final stages of the preparation of this work. Don's first paper on computer simulations of sputtering was published in 1964, long before many of us even dreamed of performing molecular dynamics on real systems. Eleven years ago Don graciously agreed to collaborate and even gave us his computer code – a beginning of an interaction that led to what we believe has been interesting science.

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1. INTRODUCTION

In the not too distant past, surface science could have been described as an emerging field of research that borrows science and engineering techniques to study surface-related phenomena. This field has sufficiently matured, however, to the point that it has spurred new techniques which are unique to the study of surfaces, and which have in turn been adapted for studying technologically important processes. Examples of fields that have been impacted by surface science include heterogeneous catalysis, bio-engineering, tribology, and semiconductor device fabrication. In fact, any technological process which involves an interface has probably benefited in some way from techniques which were developed specifically to study surfaces.

Central to the understanding of surface-related phenomena has been the study of gas-surface reactions. A comprehensive understanding of these reactions has proven challenging because of the intrinsic many-body nature of surface dynamics. In terms of theoretical methods, this complexity often forces us either to treat complex realistic systems using approximate approaches, or to treat simple systems with realistic approaches. When one is interested in studying processes of technological importance, the latter route is often the most fruitful. One theoretical technique which embodies the many-body aspect of the dynamics of surface chemistry (albeit in a very approximate manner) is molecular dynamics computer simulation.

To cover all of the contributions which molecular dynamics has made to surface science would be an almost impossible task. Instead, this review is intended as a brief survey of several areas of surface science in which we have been associated. In a sense, this chapter can be considered as a guided tour

through a small (but we hope interesting) area of theoretical surface science.

The phrase in the title 'real systems' is somewhat ambiguous and should be better defined. The theory of chemical processes is an extremely complex topic which is intertwined with other subjects, especially applied mathematics. It can, however, be conveniently divided into two steps – the development of theoretical techniques followed by their application. The former category is especially tied to applied mathematics, and will not be discussed in detail in this chapter. The second category, while relying on the first, is as equally important and often provides the ultimate test of a theoretical method. Such a test includes both the severity of any approximations used in the theory, and its ability to understand and predict phenomena which are of practical importance. It is the latter part of the test which will be emphasized in this chapter, and so 'real systems' are defined here as those which lead to an enhanced understanding of technologically important processes. This is contrasted with systems, for example, which may be sufficiently simple to be used to test the assumptions used in a theoretical method or to test a particular experimental technique, but are of limited practical importance.

1.1. Why molecular dynamics?

Molecular dynamics simulations yield an essentially exact (within the confines of classical mechanics) method for observing the dynamics of atoms and molecules during complex chemical reactions. Because the assumption of equilibrium is not necessary, this technique can be used to study a wide range of dynamical events which are associated with surfaces. For example, the atomic motions which lead to the ejection of surface species during keV particle bombardment (sputtering) have been identified using molecular dynamics, and these results have been directly correlated with various experimental observations¹. Such simulations often provide the only direct link between macroscopic experimental observations and microscopic chemical dynamics.

In its pure classical form, molecular dynamics is straightforward to carry out. One starts with given initial conditions for the system of interest. These conditions include atomic positions and velocities as well as a given interaction potential. For example, if one were simulating a sputtering event, the initial conditions might correspond to a collection of atoms which comprise the solid surface, another collection of atoms adsorbed on top of the surface, and an incoming energetic particle (Fig. 1). The atomic dynamics are then determined by numerically solving a set of classical equations of motion. Various aspects of the dynamics, such as reaction mechanisms and product distributions, can then be determined by examining the motion of the atoms during the simulation (Fig. 2). The numerical details of this type of simulation can be found in a large number of excellent reviews¹⁻⁷.

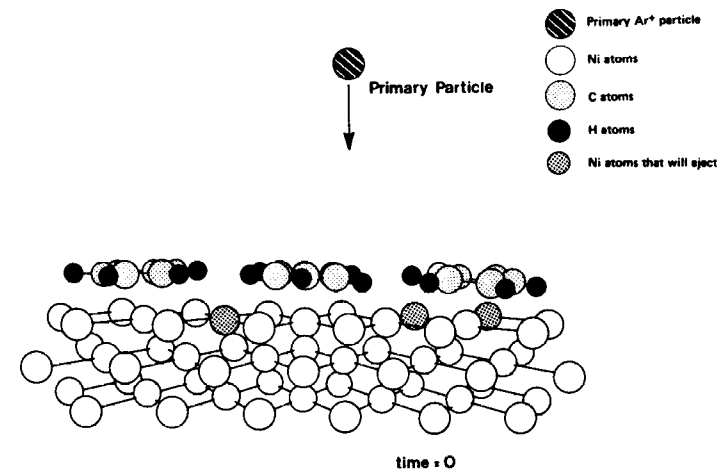


Fig. 1. Initial position of atoms before Ar⁺ ion bombardment of a layer of C₆H₆/Ni(001).

Molecular dynamics is an extremely powerful technique for understanding the atomic-scale dynamics of chemical processes. This is because it is sufficiently simple that large numbers of atoms can be treated, and because a minimal number of approximations are required. Specifically, all that is assumed is the validity of classical mechanics for the given problem and a potential-energy surface. The former approximation, although never totally true, is reasonably well understood. For example, classical mechanics describes the dynamics of heavy particles better than light particles. Hence, if one were interested in understanding the motion of hydrogen atoms, it would be understood that the classical mechanical method involves severe approximations. If one were interested in modeling the translational motion of silicon atoms, however, classical mechanics would be adequate. Potential surfaces, on the other hand, are only known well for a very few systems, and the influence which the interaction potential has on the results of a simulation is often unknown. One must therefore weigh results against the potential used. This concern is compounded for computer simulations of more than a few atoms, because the additional factor of available computer resources often demands that simple potentials be used. Because of the important role which interaction potentials play in computer simulations of real systems, they will be emphasized throughout this article.

1.2. Interaction potentials

When the results of a molecular dynamics study are being judged, the question, 'Is the potential realistic?' is often asked. This can be the incorrect question to be addressed should be, 'Is the potential used appropriate for the phenomena being modeled?'. In the same vein, it is common for a potential developed to model one property of a system to be arbitrarily extended to phenomena for which it may be inappropriate. In this way, interaction potentials are often misjudged. For example, pair potentials with tails that mimic the oscillations present in an electron gas due to ion cores can be used to understand the properties of bulk metals⁸. It is obvious that these potentials, however, would not realistically describe the interaction between three metal atoms, where an electron gas is not well defined. It is the rare interaction potential which works well for all properties of a particular system and so one needs to understand why a particular potential works well for a given property.

Computer simulation demands that interatomic potentials and their derivatives be easily evaluated. Hence, it is common practice to fit available theoretical and experimental data, such as the energetics of static structures, to simple analytic expressions. These expressions are often further refined by comparing dynamical properties calculated from a simulation with quantities measured during an experiment. For example, Garrison *et al.* have compared simulated and experimental sputtering results to refine an interaction potential for rhodium⁹. Because different energy regimes sample different sections of a potential, simulations can be effectively categorized in terms of the range of atomic interactions which the dynamics explore. With these ideas in mind, we develop the discussion in this section by dividing interactions into three regimes – short, medium and long range – and discuss how each can be effectively modeled in a computer simulation.

1.2.1. Short-range interactions

For atomic collisions of energies greater than typical bond energies (a few eV), strong repulsive forces dominate the dynamics. The general form of the potentials which describe these forces can be qualitatively understood by recalling that electron densities decay approximately exponentially outward from the nuclei. Hence, any relationships which depend on the radial structure of the electronic charge density can often be effectively described using exponential functions of the distances between atoms. Using this simple concept, analytic potentials which accurately describe the strong repulsive forces can be developed.

The repulsion between atomic cores arises primarily from two contributions. First, the 'bare' nuclei interact via simple pair-additive electrostatic

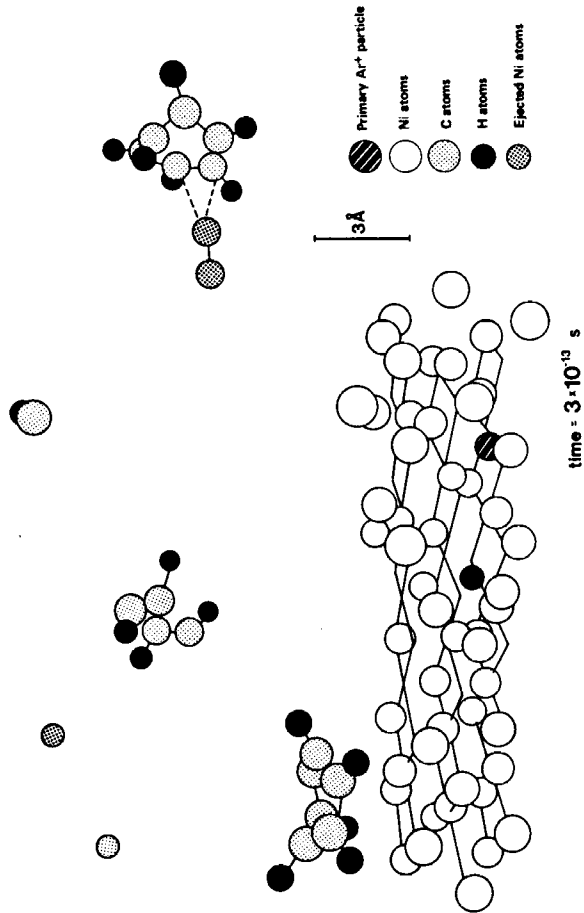


Fig. 2. Final positions of the atoms 0.3 ps after the Ar⁺ ion impact.

repulsions, where the potential is given by

$$V_{nn} = Z_1 Z_2 e^2 / R. \quad (1)$$

The quantities Z_1 and Z_2 are the charges of the two nuclei, R is their scalar separation and e is the electronic charge. To account for the shielding of the nuclear charge by the negative charge distribution of the surrounding electrons, this interaction is modified so that the effective nuclear charges are reduced as the interatomic distance increases. The form for this modified nuclear repulsion can be written as

$$V_{rep} = V_{nn} F(R) \quad (2)$$

where $F(R)$ is a 'screening' function¹⁰. If the core electronic shells do not appreciatively distort during bonding, a radially symmetric electronic screening function can be used. Bohr first proposed a simple screening function of the form

$$F(R) = \exp(-R/a) \quad (3)$$

where the quantity a is either given by

$$a = a_0 (Z_1^{2/3} + Z_2^{2/3})^{-1/2} \quad (4)$$

where a_0 is the Bohr radius, or a may be used as an adjustable parameter¹¹.

While the physical significance of Eq. (3) is apparent based on the orbital decay mentioned above, the single exponential decays too rapidly and so it is valid only for atomic separations of up to a few tenths of an angstrom. A more generally useful form of the screening function is the Molière potential, given by the screening function¹⁰

$$F(R) = 0.35 \exp(-0.3R/a) + 0.55 \exp(-1.2R/a) + 0.1 \exp(-6.0R/a). \quad (5)$$

The quantity a can either be given by the equation

$$a = 0.885 a_0 (Z_1^{1/2} + Z_2^{1/2})^{-2/3} \quad (6)$$

(called the Firsov screening) length, or a may also be taken as an adjustable parameter. A typical modification is to reduce the Firsov value by a factor of 0.8. This form was originally obtained as an analytic fit to the Thomas-Fermi calculated screening function, although the parameter a is often empirically adjusted to fit experimental results. A more detailed discussion of these screening functions, as well as a variety of others, may be found in the book by Torrens¹⁰. The Molière potential with an adjustable screening length displays realistic decay behavior over a range of energies, and so it is generally deemed to be useful.

The second source of repulsion comes from the interaction when filled electronic shells overlap and is due to the exclusion principle. Based again on the exponential decay of electron densities, it would be appropriate to assume that an exponential function of atomic distances could realistically describe

this interaction. Furthermore, based on the assumption that the filled electronic shells maintain their spherical symmetry during an atomic collision, radial pair potentials provide a simple analytic description of this interaction. A popular interaction of this type is the Born-Mayer potential of the form

$$V_{bm} = A \exp(-BR) \quad (7)$$

where A and B are adjustable parameters¹². This potential is realistic when the inner electronic shells do not overlap significantly, and so it is only useful for low-energy collisions. It is often used, however, as an adjustable repulsion which balances a many-body attraction (see below).

In conclusion, the repulsive interactions arise from both a screened coulomb repulsion between nuclei, and from the overlap of closed inner shells. The former interaction can be effectively described by a bare coulomb repulsion multiplied by a screening function. The Molière function, Eq. (5), with an adjustable screening length provides an adequate representation for most situations. The latter interaction is well described by an exponential decay of the form of a Born-Mayer function. Furthermore, due to the spherical nature of the closed atomic orbitals and the coulomb interaction, the repulsive forces can often be well described by pair-additive potentials. Both interactions may be combined either by using functions which reduce to each interaction in the correct limits, or by splining the two forms at an appropriate interatomic distance¹⁰.

1.2.2. Medium-range interactions

Medium-range interactions can be defined as those which dominate the dynamics when atoms interact with energies within a few eV of their molecular binding energies. These forces determine a majority of the physical and chemical properties of surface reactions which are of interest, and so their incorporation in computer simulations can be very important. Unfortunately, they are usually many-body in nature, and can require complicated functional forms to be adequately represented. This means that severe approximations are often required when one is interested in performing molecular dynamics simulations. Recently, several potentials have been semi-empirically developed which have proven to be sufficiently simple to be useful in computer simulations while still capturing the essentials of chemical bonding.

Solid surfaces lie at the interface of two historically distinct regimes. On the one hand, a surface can be thought of as a perturbation on a crystalline solid. Hence ideas based on the properties of condensed matter can be used to develop interaction potentials. For example, in a bulk metal the concept of a free electron gas is well developed, and simple potentials based on these ideas have been extended to include surfaces¹³⁻²⁰. Unfortunately, these ideas are

not well developed in the context of angle-dependent interactions, and so they are not exceptionally useful for describing covalent bonding.

The alternate approach to developing interaction potentials is to consider the solid surface as a very large molecule. One can then apply theoretical techniques based on gas-phase reaction ideas. The simulation of real systems, however, often requires that both reactive adsorbed atoms as well as a large number of substrate atoms be explicitly treated, and so these techniques rapidly become computationally infeasible. It is apparent that to simulate the general situation, bonding ideas from both regimes should be used. This breakdown does, however, provide a useful format within which to discuss intermediate-range interaction potentials, and so it will be used to illustrate potentials which are in current use in simulations of gas-surface interactions.

(a) Gas-phase approaches

Surfaces provide a unique environment for promoting chemistry which would not otherwise occur in the gas phase. For example, surfaces can provide a heat bath, source (or sink) of electrons, or simply a physical surrounding which brings together species which otherwise would have a low probability of meeting. If the substrate atoms do not move appreciably during the physical event of interest, and the number of atoms of interest is not too large, then few-body gas-phase potentials can be modified to model gas-surface interactions. A large number of few-body formalisms have been developed over the years^{21,22} and so rather than present an overview of all of these ideas, this discussion will emphasize general modifications used to model surface chemistry.

The spirit of this type of approach is to consider the entire surface as one body of a few-body reaction. An effective first approximation is to treat the surface as rigid, and to write all contributions of the surface to the potential energy as a periodic function of the surface lattice vectors. For example, Morse parameters which control the binding of an atom to a surface can be made a function of the position of the adsorbate within the surface unit cell²³. The advantage of this approximation is that the sum of the interactions between an adsorbed atom and each substrate atom is reduced to a single effect. A disadvantage is that because the substrate atoms are considered rigid, coupling of the reaction to thermal motion of the lattice is not included. This means, for example, that energy cannot be removed from a reaction without adding additional forces, and long-lived exothermic chemical bonding is not possible.

A correction to the rigid lattice approximation is to write the potential as a contribution commensurate with the lattice vectors as above, and to add an additional term which depends on the displacement of substrate atoms from

their lattice sites. For example, restoring forces between atoms and their atomic sites combined with correction terms to the adsorbate-surface interactions which account for the displacement of the substrate atoms have been used to modify rigid-lattice potentials^{24,25}. The advantage of this approach is that the rigid-lattice potentials, which are often simpler to fit, are easily modified to allow coupling to a heat bath.

Finally, the symmetry constraint can be removed by considering a pair sum over substrate atoms as a single contribution to the many-body energy. For example, the periodic contribution of the substrate can be replaced by a sum of contributions from each individual substrate atom^{26,27}. This allows the study of the effect of features such as amorphous surfaces, steps and defects on surface reactivity, while still retaining a potential derived from a rigid lattice. These types of potentials, however, can become time consuming in their evaluation, and can therefore be inconvenient for use in large-scale computer simulations.

(b) Condensed-phase approaches

For condensed phases of bulk metals, the binding energy can be divided into repulsions between nuclei (see above) and the interaction of the positively charged nuclei with an electron gas. Within this breakdown, the motion of the nuclei can be determined by pair-additive forces with the addition of volume-dependent terms arising from the pressure of the electron gas⁸. While computer simulations based on these types of interactions have been carried out²⁸, volume-dependent interactions are difficult to define unambiguously for surfaces.

An alternate approach, which has proven to be extremely useful for metals, has been developed by Daw, Baskes and Foiles^{13,29} (and to a lesser extent, by Ercolessi, Tosatti and Parrinello¹⁵⁻¹⁷). Called the embedded atom method (EAM) (or the glue model by the second group), the interactions in this approach are developed by considering the contribution of each individual atom to the local electron density, and then empirically determining an energy functional for each atom which depends on the electron density. This circumvents the problem of defining a global volume-dependent electron density.

While the embedded atom method has been formally derived by Daw and Baskes¹³, the functions used in computer simulations are typically empirically determined. The description presented here will therefore treat this approach as an empirical method. The first step in determining the potential is to define a local electron density at each atomic site in the solid. A simple sum of atomic electron densities has proven to be adequate, and so in most cases a sum of free atom densities is used^{13,29}. The second step is to determine an embedding

function which defines the energy of an atom for a given electron density. Finally, the attractive contribution to the binding energy produced by the function is balanced by pairwise additive repulsion interactions (see above). The expression for the total binding energy is given by

$$E_{\text{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_i \sum_j \Phi(R_{ij}) \quad (8)$$

where ρ_i is the electron density at each atomic site, $F_i(\rho_i)$ is the embedding function, and $\Phi(R_{ij})$ is the pair term arising mainly from the core-core repulsions. The function ρ_i is given by the expression

$$\rho_i = \sum_j \rho(R_{ij}) \quad (9)$$

where the quantity $\rho(R_{ij})$ is the contribution of electron density to site i from atom j , and is a function of the distance R_{ij} .

If free atom electron densities are used in the sum (9) above, the embedding function is left to determine the properties of the condensed phase. An accurate determination of this function is therefore important for modeling realistic systems. The approach commonly used is to fit this function to a large number of properties. For example, experimentally determined values of the lattice constant, sublimation energy, elastic constants and vacancy formation energies are often combined with theoretically determined relations such as the universal equation of state to provide an extensive database²⁹. This formalism has proven to provide both a realistic and easily evaluated potential which is suitable for describing a large range of properties of various pure metals and alloys^{9,13-20,30-32}. Examples of the application of the EAM to surfaces will be given below. The approach, however, is not sufficiently developed at the present time to model covalent bonding, although some progress has made by the introduction of angle-dependent electron densities³³. For covalent interactions, which determine the properties of semiconductors, other approaches based on condensed-matter ideas have been developed which have been used to model surface chemistry.

A convenient starting point for developing covalent interactions is to write the energy as a many-body expansion of the form

$$E_{\text{tot}} = V_2 + V_3 + V_4 + \dots \quad (10)$$

where the first term represents a sum over pairs of atoms, the second term represents a sum over triples of atoms, etc. A well-known example of this type of expansion, if restricted to atomic displacements near equilibrium, is the valence-force field. While this expression is exact if all terms are included, computational restrictions demand that it be truncated. In most applications, it is truncated at three-body interactions. This is partly for computational convenience and partly because the three-body term can be written in the form

of a bond bend – a concept which is physically appealing. While this approach is well developed for few-body, gas-phase reactions^{21,22}, it has only recently been extended to condensed phases.

Silicon has been the test case for potentials of this type, and so this discussion will be restricted to this element, although examples of other systems have very recently become common. The most widely used silicon potential was developed by Stillinger and Weber³⁴. The interactions used are composed of a sum of two-body and three-body terms, with the three-body interactions serving to destabilize the sum of the pair terms when bond angles are not tetrahedral. The parameters for this potential were determined by reproducing the binding energy, lattice stability and density of solid silicon, and also by reproducing the melting point and the structure of liquid silicon. Although this potential was originally developed to model liquid–solid properties, subsequent studies have demonstrated that it also provides a good description of the Si(001) surface^{35,36}. The wide applicability of this potential can be considered a testament to the care (and computer time) invested by Stillinger and Weber in its development.

A simpler potential of the form of Eq. (10) has been used by Pearson *et al.* to model Si and SiC surfaces³⁷. The two-body term is of the familiar Lennard–Jones form while the three-body interaction is modeled by an Axilrod–Teller potential³⁸. The physical significance of this potential form is restricted to weakly bound systems, although it apparently can be extended to model covalent interactions.

Brenner and Garrison introduced a potential which was derived by rewriting a valence force expression so that proper dissociation behavior is attained³⁹. Because the equations were extended from a set of terms which provided an excellent fit to the vibrational properties of silicon, this potential is well suited for studying processes which depend on dynamic properties of crystalline silicon. For example, Agrawal *et al.* have studied energy transfer from adsorbed hydrogen atoms into the surface using this potential⁴⁰.

While these potentials have been successful in modeling dynamic processes on silicon surfaces, the many-body expansion as applied in this case suffers from several drawbacks. Because all of the three potentials above have been fit to properties of the crystalline silicon solid, they implicitly assume tetrahedral bonding. Atoms on the surface of silicon are known to exhibit nontetrahedral hybridizations, and so the results for surfaces are at best uncertain. Also, none of these potentials reproduce accurately the properties of the Si₂ diatomic molecule. This again inhibits a complete description of surface reactions.

A related potential form, which was primarily developed to reproduce structural energetics of silicon, was introduced by Tersoff^{41,42} and was based on ideas discussed by Abell⁴³. The binding energy in the Abell–Tersoff expression is written as a sum of repulsive and attractive two-body interactions, with the attractive contribution being modified by a many-body term.

The stability of the diamond lattice is achieved by modifying the attractive pair terms according to local coordination, so that the atomic binding energy is at a minimum when each atom has four nearest neighbors. The parameters in this potential were determined by fitting to the properties of the Si_2 molecule, and by reproducing the binding energies and lattice constants of several crystal structures of silicon.

While the original many-body expression introduced by Tersoff (given in Ref. 41) reproduced the energy of a number of structures, it was seriously flawed because it does not give the diamond structure as the global potential minimum. Furthermore, dynamic properties of crystalline silicon are not well described, with the optic mode frequencies being too high and the nearest-neighbor radial distribution being too narrow^{42,44}. A modification of Tersoff's original potential expression which was suggested by Dodson eliminated the former flaw in Tersoff's expression⁴⁵, although it is unclear as to whether the dynamic properties are improved⁴². Finally, Tersoff has introduced a different expression which appears to have remedied both problems⁴². The Tersoff potential is expected to yield a good overall expression for silicon because it correctly describes the isolated dimer, and because it is fit to nontetrahedral structures. This means that it should provide an adequate description of silicon surfaces, although thorough testing is still being carried out⁴².

Additional silicon potentials have been introduced, but they appear to be cumbersome for studying large numbers of atoms⁴⁶. Also, several of the silicon potentials mentioned above have been modified to represent germanium⁴⁷⁻⁴⁹. These potentials are discussed elsewhere and will not be presented here.

1.2.3. Long-range interactions

The field of long-range, or intermolecular interactions is an extremely interesting and extensive topic in itself. In the context of surfaces, these forces are responsible for physisorption and can play a major role in governing processes such as rotational excitation of NO due to scattering from Ag(111)⁵⁰⁻⁵³. For the simulations discussed here, however, these interactions do not play a major role, and so discussions of this topic are deferred to a number of review articles^{54,55}.

The remainder of this chapter is devoted to describing the results of computer simulations which have used the ideas discussed above. The overall goal of these studies is to describe and understand phenomena which depend for the most part on bonding ('medium-range') interactions. For example, simulations of the reaction of small molecules on metal surfaces are discussed in section 3.1, where bond formation occurs at thermal energies. The major drawback for using simulations to study these types of processes is that the

interactions are not well known, and where a reasonable estimate can be made, analytical functional forms are complicated. Two solutions to this problem can be imagined. First, one could develop simple schemes for handling 'medium-range' interactions which still capture the essence of chemical bonding. Simulations using this type of approach will be described in section 3. The second solution would be to perform simulations where information which depended on bonding interactions was obtained, but where the dynamics probed regions of the potential which are well described using simple potentials. This is the essence of the simulations described in the next section.

2. SIMULATIONS RELYING ON SHORT-RANGE INTERACTIONS: ION-INDUCED SPUTTERING

In secondary-ion mass spectrometry (SIMS) and its sister technique fast atom bombardment mass spectrometry (FABMS), a surface is bombarded with energetic particles, and the kinetic energy of the particles converts substrate and chemisorbed atoms and molecules to gas-phase species. The ejected (or sputtered) material is subsequently interrogated using various analytical tools, such as lasers and mass spectrometers, to indirectly deduce information about the initial surface. The relationships between sputtered material and the surface, however, are not always clear, and erroneous conclusions are easily made. Computer simulations have demonstrated that a fundamental understanding of the sputtering process is required to interpret experimental data fully¹.

SIMS has traditionally been used in several regards. First, it has proven to be an important analytical tool for studying surface structures. For example, the identity as well as the velocity and spatial distributions of the sputtered material can reflect the bonding and local structure of the initial surface¹. Often this information is not easily obtained with other analytical techniques. It has also been discovered that if biomolecules are adsorbed onto a surface, FABMS can be used to convert these molecules into gas-phase species with limited fragmentation⁵⁶. This allows large molecules with atomic masses in the range of 1000–20,000 AMU to be studied on a molecule-by-molecule basis. Finally, SIMS can be used to study energy transfer between the bombarding ions and the solid. For example, recent measurements of energy- and angle-resolved neutral (EARN) data⁵⁷⁻⁵⁹ have provided experimental information with which analytic^{60,61} and simulated^{9,62} sputtering calculations can be compared.

The material sputtered from surfaces on which molecules have been chemisorbed generally consists of a collection of single atoms, strongly bound molecules, and weakly bound molecular clusters, any of which may be neutral or charged. It is often assumed, perhaps naively, that the identity and the local environment of molecules on the surface can be directly deduced from the

sputtered species. This implies that a molecule, with bond energies on the order of a few eV, can remain intact during the sputtering process. This is despite the fact that the kinetic energy of the bombarding particles is orders of magnitude larger than bond energies. This curious result, along with the total picture of the sputtering process, can be understood with the use of computer simulations.

2.1. The ejection process

As discussed in section 1, a unique feature of computer simulations is that they provide a microscopic picture of atomic motion. In the case of ion-induced sputtering, they can reveal general ejection mechanisms as well as enhance the interpretation of experimental results for specific systems. In the sputtering simulations, a set of atomic positions and velocities are chosen which mimic experimental conditions¹. In particular, the substrate is modeled by a microcrystallite which is typically five to six atomic layers deep, with each layer containing 100 to 150 atoms. When desired, chemisorbed molecules and atoms are placed at predetermined binding sites on the substrate. The dynamics are initiated by impacting the surface with an energetic particle (see Fig. 1). The kinetic energy of the impacting particle is chosen so that a relatively small number (500–1000) of substrate atoms is sufficient to effectively model the ejection process. Typical kinetic energies used are on the order of a keV. One unique feature of the sputtering simulations in contrast to other simulations of solids and liquids is the boundary conditions on the sides and bottom of the crystallite. There can easily be one or two very energetic (20–500 eV) particles that reach the edge of the crystallite. These particles in a real solid penetrate further into the bulk, damaging the sample along their path. By enlarging the crystallite in the simulations it can be verified that these energetic particles do not substantially contribute to the ejection of atoms and molecules into the gas phase. Thus these atoms are truncated from the simulation once they leave the side or bottom edge. One should *not* use periodic boundary conditions as it is nonphysical to have the energy enter the other side of the crystal. Likewise the generalized Langevin^{63–65} prescription or a rigid layer would cause reflection of the energy back into the crystal, again a nonphysical phenomenon.

Once the initial and boundary conditions are specified, the classical equations of motion are integrated as in any other simulation. From the start of the trajectory, the atoms are free to move under the influence of the potential. One simply identifies reaction mechanisms and products during the dynamics. For the case of sputtering, the atomic motion is integrated until it is no longer possible for atoms and molecules to eject. The final state of ejected material above the surface is then evaluated. Properties of interest include the total yield per ion, energy and angular distributions, and the structure and

stability of sputtered molecules. In order to further mimic experimental conditions, many trajectories are evaluated by choosing an ensemble of impact points for the energetic particle within the surface unit cell. The experiments with which the simulations are compared are performed so that the majority of the bombarded surface is undamaged¹. This makes direct comparisons between the simulated and experimental results possible.

Simulations of this type have demonstrated that the ejected species arise from energetic collisions which sample primarily the short-range repulsive part of the potential. This means that simple pairwise additive interactions can be used to describe much of the dynamics of interest without introducing overly severe approximations. This is opposed to the situation, for example, where surface damage due to the incoming ion is being examined. In this case more complicated potentials should be warranted. The sputtering simulations have used pairwise additive Molière and Born–Mayer interactions combined with attractive terms such as Morse potentials. The attractive interactions are incorporated to model the overall cohesive energy, with their exact form again not exerting a large influence on much of the dynamics of interest. Incorporation of more realistic potentials and the influence which these potentials have on the sputtering process will be discussed in section 3.2.

Molecular dynamics simulations have yielded a great deal of information about the sputtering process. First, they have demonstrated that for primary ion energies of a few keV or less, the dynamics which lead to ejection occur on a very short timescale on the order of a few hundred femtoseconds. This timescale means that the ejection process is best described as a small number of direct collisions, and rules out models which rely on many collisions, atomic vibrations and other processes to reach any type of 'steady state'. Within this same short-timescale picture, simulations have shown that ejected substrate atoms come from very near the surface, and not from subsurface regions.

These simulations have also shed light on whether the gas-phase molecules observed arise from molecules which were originally bound on the surface. In other words, are the detected molecules a direct picture of the surface? Computer simulations have clearly demonstrated that molecules such as CO and C₆H₆ can survive the sputtering process without necessarily fragmenting (Fig. 2). This is due in part to two reasons. First, the roughly equivalent effective sizes of metal substrate atoms and adsorbed hydrocarbon molecules facilitates the ejection of molecules without significant fragmentation. For example, the hard-sphere diameter for a single Rh atom in a crystal is 2.7 Å and the van der Waals diameter for a four-atom CH₃ group is 4 Å⁶⁶. This means that a moving Rh atom can 'see' this group as a single species, and can eject it without dissociating the CH bonds. The second reason for the intact ejection of large molecules is that they contain many vibrational degrees of freedom which can absorb kinetic energy that would otherwise lead to fragmentation. This contribution is especially important for the intact ejection of large biomolecules mentioned above²⁶.

The fact that molecules can survive the ion impact is encouraging for correlating gas-phase species with surface structure. Unfortunately, sputtered atoms and molecules have also been observed in the simulations to recombine into bound molecules in the near-surface region. This mechanism can lead to the detection of stable molecules which were not present on the surface, and can complicate the interpretation of experimental results. For example, the observation of NiCO and Ni₂CO clusters from the sputtering of a CO covered Ni surface could be interpreted as indicating that chemisorbed CO molecules are bound both to single Ni atoms (atop binding sites) as well as pairs of Ni atoms (bridge binding sites)⁶⁷. This could be an erroneous interpretation because recombination processes can also lead to the formation of multiply bonded CO molecules⁶⁸. The recombination mechanism, however, does not completely inhibit the ability to interpret gas-phase structures because it only occurs between species that are originally in close proximity on the surface. The general picture which simulations yield is that the identity of sputtered material can be used to identify surface species, but that one must be cautious in how far the interpretations can be taken.

One important technique which has been confirmed by simulation is the ability to deduce local bonding arrangements on the surface from the angular distribution of ejected species. The local geometry surrounding an adsorbed molecule is anisotropic. That is, along some directions a moving atom would quickly encounter a substrate atom while in other directions it would encounter an open space, perhaps between two substrate atoms along $\phi = 0^\circ$

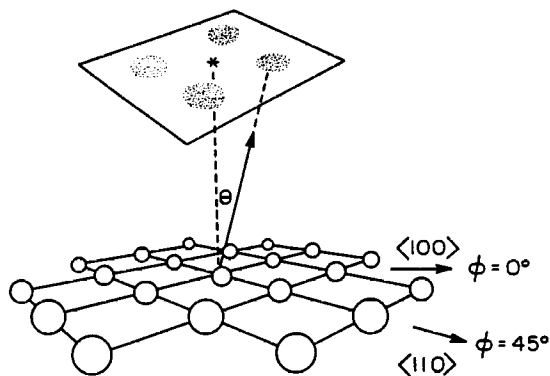


Fig. 3. Schematic representation of the angular distribution of ejected atoms from the (001) crystal face of a face-centered cubic metal. The polar angle is θ and the azimuthal angle $\phi = 45^\circ$ corresponds to the close-packed row of surface atoms. (From Ref. 1.)

of Fig. 3. This symmetric arrangement serves to direct the motion of ejected species into regions where open surface channels exist. The collective effect over the sputtering of many surface atoms is that the magnitude of the detected gas-phase species is enhanced for particular orientations. Computer simulations have been shown to agree with experimental results in regards to the angular distributions, and have confirmed this channeling mechanism⁶⁹. Furthermore, experiments have demonstrated that in most cases the angular enhancement is more dramatic for particles which eject with high kinetic energies. Again, computer simulations agree with this general conclusion, and suggest that the reason for this effect is that the higher-energy particles eject early in the collision cascade when most of the local structure is still well defined. Specific studies of this kind are discussed below.

The use of molecular dynamics simulations for understanding and interpreting SIMS experiments has been quite successful. This is despite the use of rather crude potentials, and is possible because the dynamics of interest depend primarily on the crystal structure, which is reflected in the short-range repulsion between atoms. But just as one must be cautious about carrying the interpretation of SIMS results too far, care should be taken in implying too much from this type of simulation. With the general picture of sputtering outlined above, this discussion is continued below by considering some specific details of various SIMS simulations.

2.2. Angular distributions and surface structure

The determination of the equilibrium binding sites of atoms and small molecules on metal surfaces is of central importance for understanding gas-surface reactions. Such information, however, can often only be obtained by correlating the results of many experimental techniques. For example, low-energy electron diffraction (LEED) can provide unambiguous results regarding the symmetry of a surface, but subsequent complicated current-voltage ($I-V$) analysis is needed to determine specific binding sites. Often these results are not conclusive, and additional techniques are required to confirm a result.

As mentioned above, because the local geometry surrounding a chemisorbed or substrate atom can influence its sputtering path, angle-resolved SIMS can contribute to the determination of local surface structures. It is in fact molecular dynamics calculations that first led to the idea that the destructive sputtering process can yield surface bonding information⁷⁰. The calculations predicted that the angular distributions of ejected adsorbate species such as oxygen atoms should reflect the bonding site and height on the surface⁷⁰. This observation led to the design and construction of an angle-resolved secondary ion mass spectrometry (SIMS) apparatus⁷¹.

Continued interplay between experiment and theory has prompted the development of a new method to measure the energy- and angle-resolved

neutral (EARN) atom distributions^{57-59, 72}. In this technique, ejected neutral atoms are ionized by a laser above the surface. Because the ionization of the sputtered neutral atoms takes place at a different point in the trajectory than the atoms which are ionized during the SIMS processes, an applied potential bias serves to separate the two types of ejected species. This latest development now allows direct comparisons between predicted and measured particle trajectories. Previous to the EARN experiments, the SIMS experiments measured *ion* distributions while the calculations described the *neutral* distributions. The ability to make detailed and direct comparisons between the molecular dynamics model and the measured energy and angle distributions of neutral particles that eject during keV ion bombardment has provided the impetus for significantly expanding the scope and applications of the molecular dynamics technique. Below are given four examples of how combined experiment and molecular dynamics calculations have provided insight into bonding geometries on surfaces. The first two are EARN experiments on clean and oxygen-covered Rh(111) in which neutral Rh atoms are detected, and the latter two are SIMS experiments in which ions are detected.

2.2.1. Clean Rh(111)

The first detailed comparison between EARN data and molecular dynamics simulations was on Rh(111). The initial simulations were performed using a pairwise additive potential⁷³. The polar angle distributions from both the calculations and experiment are shown in Fig. 4. The azimuthal angles are defined at the top of the figure. Examination of the pair-potential results (right-hand side of the figure) reveals overall semiquantitative agreement between the calculated and measured distributions. The peak intensity along the azimuthal direction $\phi = -30^\circ$ is greater than along $\phi = +30^\circ$ or 0° for all secondary-particle energy ranges. As the particle energy increases, the $\phi = +30^\circ$ intensity increases relative to the $\phi = 0^\circ$ intensity. Both theory and experiment find that the intensity at $\theta = 0^\circ$ relative to the peak intensity ($\theta = 25-40^\circ$) increases as the Rh atom energy increases. The agreement between the measured and calculated distributions is quite remarkable as pair potentials were used, and no adjustment of the parameters in conjunction with this experimental data was performed. Obviously, the pair potential description is a reasonable first approximation to describe the ejection events. The reason for this agreement is that much of the ejection process is dominated by the surface structure and not the details of the interaction potential. Of note is that the pair potential does very well at reproducing the azimuthal anisotropy. There are discrepancies between the experimental and calculated results which can be removed by using a many-body EAM interaction potential in the simulations. These results are discussed in section 3.2.

It is very difficult experimentally to determine the positions of the second-

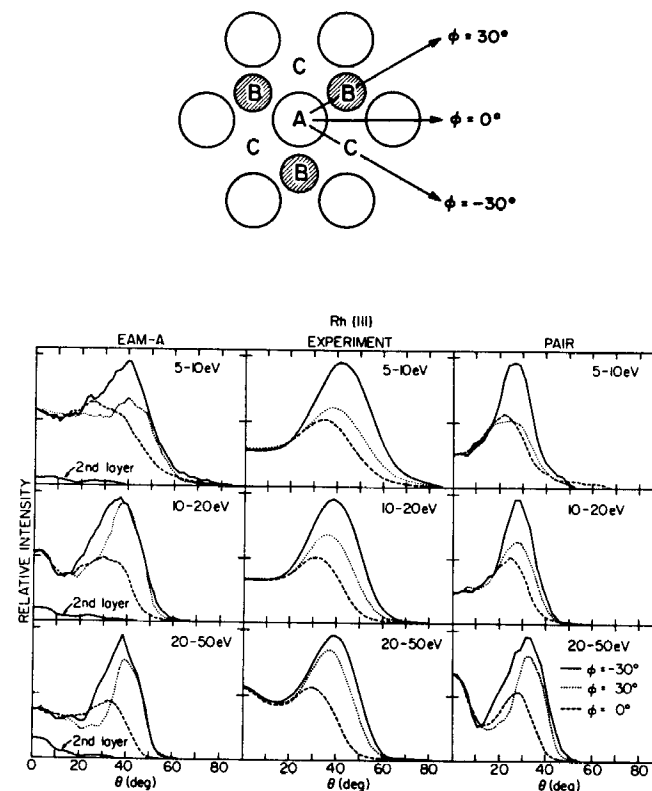


Fig. 4. Polar angle distributions for various azimuthal angles for fixed secondary kinetic energy of the Rh atoms. In each frame the data are normalized to the $\phi = -30^\circ$ peak intensity. For the calculated data the full width at half maximum (FWHM) of the resolution is 15° in the polar angle. A constant solid angle is used in the histogramming procedure. The experimental resolution is approximately the same. The surface normal corresponds to $\theta = 0^\circ$ and $\theta = 90^\circ$ is parallel to the surface. The curve marked '2nd layer' is the polar distribution along $\phi = -30^\circ$ for the ejected second-layer atoms. The azimuthal directions are defined above. Open circles designate first layer atoms and shaded circles second-layer atoms. The letters A, B, and C designate possible adsorption sites for oxygen atoms. (From Ref. 9.)

layer atoms in the Rh(111) (or any face-centered cubic(111)) face. Note that there is a six-fold rotation axis (Fig. 4) if only the surface atoms are considered but that if the second-layer atoms are considered there is a three-fold rotation axis. With LEED it is difficult to determine the placement of the second-layer atoms without a detailed I - V analysis. With the EARN experiment in conjunction with the simulations the determination of the absolute crystal orientation is straightforward. The sputtered intensity along $\phi = -30^\circ$ is greater than along $\phi = +30^\circ$. This ambiguity in placement of the second-layer atoms carries over to the placement of adsorbates on the surface. For example, oxygen atoms tend to bond in high-coordination sites, for example, the three-fold hollow sites on Rh(111). However, there are two such sites, one where the oxygen atom would be directly above a second-layer atom (B-site) and one where the oxygen atom would not be above a second-layer atom (C-site). In the following section we show how the EARN distributions in conjunction with the calculations can determine both the site and coverage of oxygen on Rh(111).

2.2.2. Oxygen-covered Rh(111)

Oxygen adsorbs atomically on Rh(111) at room temperature in an ordered overlayer structure that yields a (2×2) LEED pattern⁷⁴. There are at least two structural unknowns for this system – one that involves coverage and one that involves adsorption site. A simple (2×2) structure with one adsorbate atom per unit cell results in a 0.25 monolayer coverage, that is, one oxygen atom per four Rh surface atoms. However, if there are three domains of a 0.5 monolayer coverage in an arrangement where each domain would yield a (1×2) pattern, the resulting overlapping LEED pattern looks like a (2×2) . Thus the adsorbate coverage is not apparent from the LEED pattern. Second, oxygen is generally believed to adsorb in three-fold hollow sites on the Rh(111) surface. As shown in Fig. 4 there are two three-fold hollow sites on the (111) surface, one above a second-layer atom (B-site) and one not above a second-layer atom (actually above a third-layer atom (C-site)). To distinguish between these two three-fold sites experimentally is extremely difficult. In the EARN distributions intuition indicates that if an oxygen atom is adsorbed in a C-site then it should preferentially attenuate ejection in the $\phi = -30^\circ$. If it is adsorbed in the B-site, however, it would preferentially attenuate ejection in the $\phi = +30^\circ$ direction.

The EARN distributions of Rh atoms ejected from O/Rh(111)- (2×2) have recently been measured⁷⁵. In addition simulations were performed for the oxygen atoms in both of the three-fold sites and for both the 0.25 and 0.5 monolayer coverages. Experimentally the Rh atom yield decreases by about a factor of two with the oxygen adsorption. To reproduce this effect in the simulations the 0.5 monolayer coverage was required. In the experimental

EARN distributions the yield along the azimuth $\phi = -30^\circ$ was preferentially reduced with respect to $\phi = +30^\circ$. In agreement with intuition, the calculations confirm that the oxygen atom resides in the C-site. Thus from the cooperation of EARN experiments and computer simulations the coverage and nature of the adsorption site of O/Rh(111) has been determined. It will be of interest to see if other surface structure techniques can be used to confirm these specific surface structures.

2.2.3. Pyridine versus benzene

In addition to the enhancement of sputtering yields for specific azimuthal angles, structure in the polar (defined from the surface normal) angular distributions can also be used to determine bonding geometries. When benzene and pyridine molecules are adsorbed at low coverages on a Ag(111) surface, molecule-surface bonding can occur through the molecular π -cloud. This results in the molecules lying flat on the surface. As the molecular coverage is increased, however, the molecules become 'crowded' and repel one another. For the case of benzene, the π -bonding is stronger than the repulsive intermolecular forces, and the molecules remain flat on the surface. Pyridine, however, can also σ -bond to the surface through the N atom, and so the rings can lift from the surface while leaving the N atom σ -bonded⁷⁶. The net effect of increasing pyridine coverage is therefore thought to lead to a 'standing' orientation of the molecules. It was believed that this orientation would effect the angular distributions of sputtered molecules, and so a combined computer simulation-SIMS study was undertaken⁷⁷⁻⁷⁹.

Computer simulations of the sputtering of benzene and pyridine molecules suggest that the molecular orientation influences the sputtering dynamics in two respects⁷⁹. First, it was observed that the π -bonded rings often eject intact, while the upright σ -bonded rings have a very small cross-section for molecular desorption. The second effect observed is that polar-angle distributions are sharper for the σ -bonded molecules than for the π -bonded molecules. This is a result of the channeling of ejected molecules upward by their upright neighbors, a process which does not occur for the π -bonded molecules. Furthermore, it appeared that particles ejected with low kinetic energy showed sharper distributions than those ejected with higher kinetic energies. This is different from the case of azimuthal-angle enhancements, where the higher-energy particles reflect the symmetry of the initial environment of the sputtered species better than low-energy particles. The reason for this difference is that the upright molecules are easily moved, and so molecules with high kinetic energy distort the local environment more than low-energy particles, and thus have broader polar distributions.

The SIMS experiments were performed by sputtering both adsorbed benzene and pyridine at various coverages from Ag(111) surfaces^{77,78}. For

increasing coverages of pyridine, and presumably increasing 'upright angle', a decrease in the intensity of sputtered intact molecules was observed. This is consistent with the dynamics predictions, where again decreased molecular ejection was observed for standing configurations of pyridine over the π -bonded benzene molecules. In addition, experimental polar-angle distributions showed agreement with the dynamics results. For the sputtering of benzene and low coverages of pyridine, the angular distributions were relatively broad. As the pyridine coverage was increased, however, the polar distributions for the ejected pyridine molecules became more sharply peaked, with low-energy molecules showing slightly sharper peaks than those ejected with high energies. Both of these effects were predicted by the dynamics calculations, and are easily understood based on the molecular orientation of the molecules on the surface.

2.2.4. CO on Ni(7 9 11)

Steps and defects are thought to exert a large influence on the chemical reactivity of surfaces, and so an understanding of the role which they play in the binding of adsorbates is important. When surfaces containing atomic steps are sputtered, it would be expected that the azimuthal angle of the incident ion beam would affect the sputtering results. For example, an ion beam that was angled so that the bottom of a step was bombarded would be expected to 'peel off' more surface atoms than one that was angled to bombard the top of a step. This would lead to an enhancement of the ion yield for certain azimuthal angles of the ion beam. Similarly, if adsorbates showed preferential bonding to the top or bottom of a step, the sputtering yield or molecular clusters would also show an azimuthal-angle dependence of the ion beam. To test this hypothesis, a combined SIMS and computer simulation study of the adsorption of CO on a stepped Ni(7 9 11) surface was undertaken⁸⁰.

The Ni(7 9 11) surface explored in this study was composed of terraces with (111) orientation five atomic rows wide separated by steps of monatomic height with (110) orientation. An ensemble of surface science techniques have suggested that adsorbed CO molecules on this surface preferentially bond to sites at the bottom of the steps at low coverages and temperatures^{81,82}. At higher temperatures and coverages, however, the CO molecules are thought to bind both at the steps and on the terraces. At the bottom of the step two bridge sites are accessible, with one being two-fold coordinate and the other three-fold coordinate. The occupation of both sites had been suggested based on previous studies.

In the SIMS experiment the CO covered Ni surface was sputtered using an ion beam whose azimuthal angle could be varied⁸⁰. The ion yields for various ejected species were found to vary with sputtering angle, with the greatest sensitivity being shown by sputtered NiCO⁺ clusters. For low coverages, the

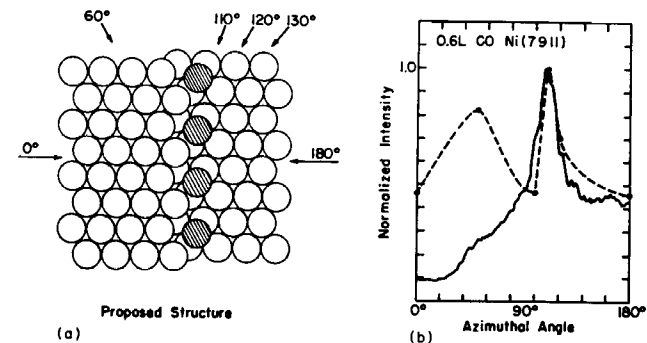


Fig. 5. Ni(7 9 11) with adsorbed CO. (a) Proposed structure. The open circles represent Ni atoms and the shaded circles are CO molecules. The numbers refer to the incident azimuthal angle of the primary ion. (b) NiCO⁺ intensity versus azimuthal angle of the bombarding Ar⁺ ion. The nickel surface was exposed to 0.6 L of CO. The solid line represents the experimental data and the dashed line results from the classical dynamical calculation. The additional peak at $\phi = 60^\circ$ is not yet understood. (From Ref. 1.)

yield of the NiCO⁺ ions with the ion beam aligned towards the bottom of the step (180° in Fig. 5) was found to be twice that with the beam aligned down the step (0° in Fig. 5). This result confirmed the concept of using aligned ion beams to study the structure of adsorbates at steps. An additional feature of the results was a sharp peak in the NiCO⁺ distribution for the Ar⁺ azimuthal angle of incidence of ~120° (Fig. 5). This feature disappeared for higher coverages, and so appeared to be a signature of the binding site of the CO molecules.

Computer simulations were performed for CO molecules adsorbed at the two proposed sites at the bottom of the step and for CO molecules adsorbed in bridge sites on the terrace⁸⁰. The experimental results for low CO coverages could only be reproduced for the CO molecules adsorbed at the two-fold bridge site at the bottom of the step. However, no distinct formation mechanism for the sputtered NiCO species which contributed to the signature peak could be discerned. The only general trend seemed to be that these species were not composed of CO and Ni atoms which were originally bound on the surface, but formed via recombination in the near-surface region.

As demonstrated in this section, the agreement between simulation and experimental results for keV particle bombardment of solids is remarkable. This is especially true when one considers the rather crude potentials used in the calculations. To understand the reason for this agreement, the underlying features of the dynamics should be reviewed. The surface structures which are

deduced from experiment are clearly caused by complicated many-body interactions. 'Guesses' for these structures enter into the simulations as initial conditions, and if left to evolve under the influence of the pair-additive potentials, the atoms would undoubtedly collapse into nonphysical configurations. The sputtering process, however, occurs much faster than these relaxations (10^{-13} s), and so the repulsive collisions dominate the dynamics. Again, for this regime pair-additive potentials are often adequate. Since the final atomic positions and velocities of the sputtered material reflect the initial configurations, structures which depend on complicated many-body interactions are deduced using simple short-range forces. This is the key to understanding the SIMS and EARN simulation results.

Several topics which are important to the keV particle bombardment processes have not been discussed here. Foremost is the ionization probability for sputtered species. In the traditional SIMS mode, only those species which eject charged are detected whereas in the simulations the motions of neutral species are determined. This complication is currently being overcome in two ways. First, models which include ionization effects have been incorporated into dynamics simulations^{83,84}. While this is the obvious approach, the appropriate manner in which to treat the ionization problem is not clear. The second approach is to ionize sputtered neutral atoms after ejection in the experiment, and to study the properties of these ions. The significant progress recently made using lasers to post-ionize sputtered neutral atoms was discussed above and results deduced in this way have led to an enhanced understanding of ion-surface energy transfer⁵⁷⁻⁵⁹. A second topic which has not been addressed here is the influence which the surface image charge has on the trajectories of sputtered ions. This is a relatively simple effect to study, and simulations have been performed which mimic these forces⁸⁵. Finally, the enhanced agreement with experiment through the use of more realistic potentials has not been explored. Studies of this type, along with comparisons with data for post-ionized sputtered neutral atoms, are discussed in the next section.

3. SIMULATIONS RELYING ON REALISTIC MEDIUM-RANGE INTERACTIONS

In this section examples of classical dynamics simulations where the kinetic energies of the atoms involved are on the order of typical bond energies are discussed. This energy regime is more difficult to model than the higher-energy dynamics discussed in the previous section because the many-body nature of the forces strongly governs the dynamics. Most chemical reactions of interest, however, take place in this energy regime, and so considerable effort has gone into studies of this type.

In section 3.1, reactions of diatomic molecules with metal surfaces are discussed. These studies, although perhaps not sufficiently complicated to directly address processes of technological interest, have produced considerable insight into the dynamics of gas-surface reactions. Simulations of metal surfaces where more realistic interactions are required than are used in the gas-surface studies are presented in section 3.2. This is followed in section 3.3 by a discussion of simulations of reactions on the surfaces of covalently bonded solids. These final studies are particularly suited for addressing technologically relevant processes due to the importance of semiconductor technology.

3.1. Reaction of gas-phase molecules with metal surfaces: modified LEPS potentials

The exchange between the gas-phase and chemisorbed states of small molecules plays a vital role in such technologically important fields as heterogeneous catalysis and corrosion. The dynamics involved in these processes, however, are not currently well understood. Molecular-beam studies combined with classical trajectory calculations have proven to be a successful tool for understanding the underlying features of atomic-scale motion in the gas phase. The extension of these techniques to surfaces has also helped in elucidating the details of gas-surface reactions.

One formalism which has been extensively used with classical trajectory methods to study gas-phase reactions has been the London-Eyring-Polanyi-Sato (LEPS) method^{86,87}. This is a semiempirical technique for generating potential energy surfaces which incorporates two-body interactions into a valence bond scheme. The combination of interactions for diatomic molecules in this formalism results in a many-body potential which displays correct asymptotic behavior, and which contains barriers for reaction. For the case of a diatomic molecule reacting with a surface, the surface is treated as one body of a three-body reaction, and so the two-body terms are composed of two atom-surface interactions and a gas-phase atom-atom potential. The LEPS formalism then introduces adjustable potential energy barriers into molecule-surface reactions.

Although the theoretical roots of this technique are very well established, it is more often used as a flexible surface which can be adjusted to fit either experimental data or data established by better electronic-structure methods. The LEPS formalism has also been extensively used to explore the relationships between the potential energy surface and the details of chemical dynamics⁸⁷. Because of the widespread use of this potential for studying gas-phase reactions, the specific form of the equations will not be discussed here. The interested reader is instead referred to references which discuss this approach in more detail^{23,86,88}.

3.1.1. Hydrogen-metal reactions

Exchange reactions of $H + H_2$ (or H_3) have provided the testing ground for theoretical methods which are used to understand gas-phase chemical dynamics⁸⁹. Interest in modeling the reaction of hydrogen with metal surfaces is therefore not unexpected. In addition, hydrogen often plays an important role in reactions associated with catalysis, so studies of this type also have practical application.

Several researchers have used modified forms of the LEPS potential (see section 1.2 for a discussion of the modifications) to study the dynamics of H_2 on the surfaces of various metals. Initial studies of this type were restricted to rigid surfaces, and the parameters in the LEPS surfaces were either determined by fitting to available experimental or theoretical data, or systematically varied to produce potential energy surfaces with specific properties.

In a series of studies, McCreery, Wolken and coworkers have used a LEPS potential to model reaction of H_2 and HD with the W(001) surface^{23, 90, 91}. The substrate in these studies was restricted to be rigid, and Morse functions were used for the hydrogen-surface and H_2 two-body interactions. The parameters in the Morse functions were determined for single hydrogen atoms adsorbed on the tungsten surface by fitting to extended Hückel molecular orbital (EHMO) results, and the H_2 Morse parameters were fit to gas-phase data. The Sato parameter, which enters the many-body LEPS prescription, was varied to produce a potential barrier for the desorption of H_2 from the surface which matched experimental results.

Using their H_2 -W potential, McCreery and Wolken have modeled the recombination and desorption of two H atoms that are initially adsorbed on the surface⁹⁰. These simulations were initiated by dividing 3.5 eV of translational energy between the two adsorbed atoms. Classical equations of motion were then integrated until desorption was observed, or it was determined that both atoms would remain on the surface. They reported that 3.4% of the atomic collisions resulted in the desorption of an H_2 molecule. An analysis of the initial translational energies of two hydrogen atoms showed that this mode was enhanced for cases where the two atoms had similar energies. They also reported that 4.6% of the collisions resulted in the desorption of only one of the hydrogen atoms. This mode of reaction was enhanced when one of the atoms possessed almost all of the initial energy. Desorption of both hydrogen atoms into isolated gas-phase species was not possible, since the total energy was insufficient to reach this state.

Energy and angular distributions for the desorbed species were also analyzed. The polar angular distributions for all species were reported to be peaked toward the surface normal, and did not have the cosine form which is indicative of thermal processes. This was shown to result because atoms which approach at large impact parameters along the surface do not react. This

orientation would lead to desorption with large polar angles, and so this region of the distribution was depleted. They also showed that the distribution of energy among the degrees of freedom of the desorbed H_2 molecules matched those predicted by statistical theories^{92, 93}.

Elkowitz, McCreery, and Wolken have also examined the reaction of a gas-phase hydrogen atom with a hydrogen atom initially adsorbed on the tungsten surface using the same LEPS function⁹¹. They report that for an initial energy of the incoming hydrogen atom of 0.44 eV, 1.3% of the collisions resulted in the desorption of a hydrogen molecule, while 12.8% led to the desorption of one of the atoms. Furthermore, they report that in a vast majority of cases the atom initially on the surface remains adsorbed unless molecular desorption occurs, and the reflection of the incoming atom tends to be unaffected by the presence of the surface species. Unlike the combination and desorption of the two atoms initially on the surface, they report that the energy distribution of the desorbed H_2 molecules is not well described by statistical theories.

McCreery and Wolken have also extended their model by exploring the effect of various potential energy surfaces on the dynamics of hydrogen atoms on a metal surface, and by extending the LEPS prescription so that three atoms adsorbed on the surface could be modeled⁸⁸. Varying heights of the potential barrier were used to explore the relationships between the chemical dynamics of reaction and the potential surface for the chemisorption of H_2 molecules^{94, 95}. For large barrier heights, they found that translational energy was more effective in promoting the chemisorption of the H_2 molecule than was internal energy. The topology of the potential surface was further changed in a study of the combination and desorption of H_2 from this surface by varying both the barrier heights and relative exothermicity of the reaction²³. In both of the dynamics studies, the populations of various energy modes and their relationships to the chemical dynamics agreed with trends predicted by gas-phase studies, and so the application of gas-phase models to gas-surface reactions was verified.

Other researchers have used LEPS plus rigid-surface potentials to study the reaction of H_2 with metal surfaces. Gelb and Cardillo have used a LEPS potential to model the reaction of gas-phase H_2 molecules with Cu(001) and Cu(011) surfaces⁹⁶⁻⁹⁸. Their studies have suggested that a 'rough' surface (that is, one with a high barrier for surface diffusion) is needed to match experimental molecular-beam results⁹⁸. Furthermore, they reported that increased translational and vibrational energy of the incoming H_2 molecule enhances the probability of dissociative adsorption, while rotational energy was ineffective in promoting reaction.

In efforts to improve upon the LEPS scheme outline above, other prescriptions for the single atom-surface interaction have been formulated. The initial studies using the LEPS approach modeled the atom-surface interaction as a two-body term where the parameters used in the function are

dependent on the position of the atom within the surface until cell. These interactions are not transferable between different crystal faces, and they do not allow the study of amorphous surfaces or surfaces which contain defects. Purvis and Wolken have addressed this problem by proposing that the atom-surface two-body term that enters the LEPS formalism be replaced with a sum of two-body terms between the adsorbed atom and the surface atoms²⁷. This modification allows the study of surfaces which do not possess periodicity. Lee and DePristo have further extended the LEPS formalism by replacing the two-body atom-surface interaction with other more realistic many-body interactions^{99,100}. These relatively complicated functions combined with the LEPS formalism have produced potential energy surfaces which are transferable between crystal faces, and which can be adjusted to reproduce dynamical results.

Another advance in the LEPS description of H₂-metal surface dynamics has been the introduction of moving substrate atoms¹⁰¹⁻¹⁰³. The use of a static surface can be justified on the basis of the difference in mass between the hydrogen atoms and the metal atoms. The substrate atoms are sufficiently heavy compared to the hydrogen atoms that they do not have sufficient time to move during much of the dynamics of interest. For multiple collisions, however, the timescale of reaction becomes longer, and including substrate atoms which can adjust to the influence of the motion of the molecule can be important. This motion can change the features of the potential energy surface, and conclusions drawn from rigid surface studies may be affected. Furthermore, energy transfer between the H₂ molecule and the substrate is not incorporated with rigid surfaces, and so moving substrate atoms are necessary to produce long-lived trapping of an incoming adsorbate on the surface.

The initial studies which incorporated moving substrate atoms used correction terms to the rigid-surface LEPS potential functions, and did not specifically include temperature effects in the dynamics of the substrate^{101,103}. Further studies, however, incorporated the generalized Langevin equations⁶³⁻⁶⁵ into the equations of motion governing the dynamics of the substrate. This advance introduced a realistic temperature-regulated response of the substrate to the surface dynamics without significantly increasing the number of atoms explicitly entering the simulation. It also reduces the number of approximations which may affect dynamical results, and allows the study of systems where the mass of the reacting surface atoms is comparable to the atoms in the substrate.

Studies of H₂ have proven the feasibility of using the LEPS formalism to study gas-surface reactions, and have indicated that relationships between the potential surface and chemical dynamics derived from gas-phase studies can be generalized to reactions with surfaces. Reactions of H₂, however, represent simple systems compared even to other diatomic molecules, and extensions to other more complicated reactions are rare. A few studies of other diatomic

molecules interacting with metal surfaces have been undertaken, and the results of these studies have helped in elucidating the dynamics of complicated surface reactions.

3.1.2. Nitrogen, oxygen and carbon monoxide-metal reactions

The chemical reactions of N₂, O₂ and CO on metal surfaces are the ones that have received the most attention both from experimentalists and theorists. Kara and DePristo have examined the dissociative chemisorption of N₂ on the W(011) surface using the combination many-body atom-surface interactions plus LEPS potential formalism¹⁰⁴ which was developed by Lee and DePristo to model H₂ adsorption¹⁰⁰. For this system, molecular beam studies have demonstrated that the probability of dissociative chemisorption scales with the normal component of the initial translational energy for large incoming polar angles, but it scales with total energy for angles between 0° and 45°¹⁰⁵. This is different from most other cases, where the probability for reaction depends on the normal component at all angles. Kara and DePristo demonstrated that the energy scaling for dissociative chemisorption could be understood based on the width of the transition state at the potential energy barrier. For a narrow transition state, their results show that the probability for dissociative chemisorption scales with total kinetic energy. This is because a restricted atomic configuration is required to overcome the barrier, and so the energy must redistribute (with a sufficient amount of energy entering the bond stretching mode) for reaction to occur. For a wider barrier, however, the molecule is less restricted, and so the normal contributions to the translational energy is directly converted to the stretching of the N—N bond. This leads to dissociation of the bond and chemisorption. This study demonstrates the ability of the LEPS formalism to be adjusted so that the characteristics of reaction can be correlated with features of the potential energy surface.

Another system which displays complex behavior is the reaction of oxygen on silver. For the Ag(011) surface, O₂ displays molecular adsorption at substrate temperatures below 185 K¹⁰⁶⁻¹⁰⁹, and dissociative chemisorption at substrate temperatures between 185 K and 600 K¹⁰⁶⁻¹¹³. Furthermore, overlayers of chemisorbed oxygen atoms produce (*n* × 1) structures, where *n* varies from 7 at low coverage to 2 at the highest coverage¹¹¹⁻¹¹³. The low coverage (7 × 1) surface structure is composed of rows of oxygen atoms that are separated by 20 Å. This implies a long-range repulsive force between the atoms along the direction between rows, and a shorter-range interaction between atoms within the rows. Both experimental and theoretical studies have suggested that the physical origin of this interaction is a transfer of electron density from the solid to the adsorbates which leaves the oxygen atoms with a net negative charge^{106,108,109,114,115}. This charge apparently results in an anisotropic long-range repulsion between adsorbed atoms.

In an effort to model this system, Lin and Garrison modified the LEPS prescription to include a long-range anisotropic force between adsorbed oxygen atoms^{11,6}. The oxygen-surface bonding interactions were modeled by a Morse function which has parameters that depend on the position of the oxygen atom in the surface unit cell. The oxygen-oxygen two-body interaction was also modeled using a Morse function. The anisotropic contribution to the potential was incorporated into the two-body oxygen-oxygen antibonding interaction that enters into the LEPS formalism. A long-range $1/R$ (where R is the scalar distance between atoms) dependency was used for the component of this interaction in the direction between rows, while a shorter-range exponential function was used in the direction within the rows. This resulted in an oxygen-oxygen interaction which produces the $(n \times 1)$ structures for varying coverages. Also, because it enters the antibonding two-body interaction (instead of the bonding interaction) in the LEPS prescription the long-range interaction does not change the gas-phase characteristics of the O_2 molecule.

The parameters in the O_2 -Ag LEPS potential were determined by fitting to a variety of experimental data, and the surface was restricted to be rigid. Two different potential energy surfaces were tested, both of which were consistent with the available data, but which differed in bonding characteristics for the O_2 molecule. For the first potential function, classical dynamics trajectories showed that both molecular and atomic adsorption were possible, while for the other the reaction of O_2 resulted only in dissociative chemisorption. Both potentials, however, displayed sticking probabilities which are strongly dependent on the orientation of the molecule with respect to the surface. Although the results are somewhat inconclusive due to the lack of sufficient data to determine a unique potential surface, this study did demonstrate that the LEPS formalism can be modified to include long-range electrostatic interactions. This suggests that the LEPS approach can be sufficiently flexible that the dynamics of complicated systems can be modeled.

The reaction of CO with platinum is an example of another complicated and technologically important system which has been studied using the LEPS formalism. Tully has modeled the abstraction of a chemisorbed C atom from the Pt(111) surface by a gas-phase O atom using a LEPS potential and a dynamic surface^{11,7}. This abstraction reaction is exothermic, and so Tully was interested in the partitioning of the energy released by the reaction. The parameters entering the potential surface were determined from a variety of experimental measurements, and realistic temperature effects were included by using a generalized Langevin equation to govern the motion of the lattice atoms.

The classical trajectories were initiated with the C atom on the lattice near the lowest-energy binding site, and the O atom heading toward the surface aimed in the vicinity of the C atom. The exothermicity of the reaction

combined with the small barriers in the potential surface resulted in a large reaction probability. Furthermore, Tully reported that most of the energy of reaction is carried away by the desorbing molecule rather than being deposited into the surface. He reports an approximate ratio of energy deposited into translational, vibrational and rotational modes of the CO molecule of 2:2:1. Although he cautions that uncertainties in the potential energy surface makes this ratio inconclusive, variations of the potential within reasonable limits are reported to still result in the majority of the released energy being carried away by the CO molecule.

The modification of theoretical gas-phase reaction techniques to study gas-surface reactions continues to hold promise. In particular, the LEPS formalism appears to capture a sufficient amount of realistic bonding characteristics that it will continue to be used to model gas-surface reactions. One computational drawback of the LEPS-style potentials is the need to diagonalize a matrix at each timestep in the numerical integration of the classical equations of motion. The size of the matrix increases dramatically as the number of atoms increases. Many reactions of more direct practical interest, such as the decomposition of hydrocarbons on metal surfaces, are still too complicated to be realistically modeled at the present time. This situation will certainly change in the near future as advances in both dynamics techniques and potential energy surfaces continue.

3.2. Metals: the embedded-atom method

The structure and dynamics of clean metal surfaces are also of importance for understanding surface reactivity. For example, it is widely held that reactions at steps and defects play major roles in catalytic activity. Unfortunately a lack of periodicity in these configurations makes calculations of energetics and structure difficult. When there are many possible structures, or if one is interested in dynamics, first-principle electronic structure calculations are often too time consuming to be practical. The embedded-atom method (EAM) discussed above has made realistic empirical calculations possible, and so estimates of surface structures can now be routinely made.

Prior to the development of the EAM¹³⁻¹⁷ a majority of simulations of metals and metal surfaces used pair-additive potentials. These potentials, however, rarely yield a good description of most metals. For example, if the parameters entering a typical pair potential are determined from an isolated diatomic molecule, the binding energy for the metal is generally overestimated, and the lattice constant is usually too small. To circumvent this problem, pair terms can be fit to properties of the bulk metal without regard to the isolated dimer molecules^{11,8}. Although lattice constants and binding energies can be reproduced this way, other properties (particularly those of small clusters) are

often meaningless. For example, pair potentials generally predict an outward expansion of surface layers, while surface relaxations for most metals involve a contraction.

The EAM has been widely used to predict and understand the structure of the surfaces of metals. One system that has been thoroughly studied is gold. Ercolessi, Parrinello and Tosatti (and also Dodson¹⁹) have used the EAM to determine a likely structure for the reconstruction of the Au(100) surface^{15,16}. Using molecular dynamics to relax the surface, Ercolessi *et al.* determined that a (35×5) reconstruction of this surface is the lowest energy structure. This observation is very similar to a (5×1) structure reported by Dodson¹⁹. This reconstruction is a result of a rearrangement of surface atoms into a more densely packed configuration, and also involves a relaxation of the first few atomic planes below the surface. Both Ercolessi and Dodson report quantitative agreement with experimental observations, including scanning-tunneling microscopy results¹⁹.

Garofalo, Tosatti and Ercolessi have also studied the structure of the Au(110) surface using the same method¹⁷. For this surface, their molecular dynamics studies gave a (1×2) missing row geometry as the lowest-energy structure. This result is in agreement with both experimental evidence¹²⁰⁻¹²⁵ and other theoretical calculations^{126,127}. They also found that other similar missing row structures are very close in energy, and that the appearance of these other structures at finite temperatures may account for additional experimental observations.

The EAM has been used to study the surface structure of other metals and metal alloys. For example, Daw has suggested that a missing row configuration is also the likely structure for the (2×1) reconstruction of the Pt(110) surface¹⁴. Studies have also been made of the surface structures of various alloys, where for example surface segregation of one constituent over the other has been observed^{20,128-130}. In addition to studies of specific systems, the EAM formalism is also sufficiently general that it has been used to understand trends in surface reconstructions among various metals^{131,132}.

The EAM method has proven to provide structures and energetics at thermal energies which agree with experiment for a large number of metals. Simulations of atomic dynamics at higher energies, however, have been fewer in number. In section 2 the case was made that pair potentials are generally adequate for describing the short-timescale dynamics involved in sputtering. Some of the results of the simulations, however, are very dependent on the potential. For example, the yield of Rh_2 ejected from Rh(111) is impossible to determine using pair potentials that describe only the bulk energetics. This has created interest in using the EAM formalism to determine potential functions which can be used at a variety of energies, and which describe both few-atom clusters as well as the bulk metals^{32,133,134}.

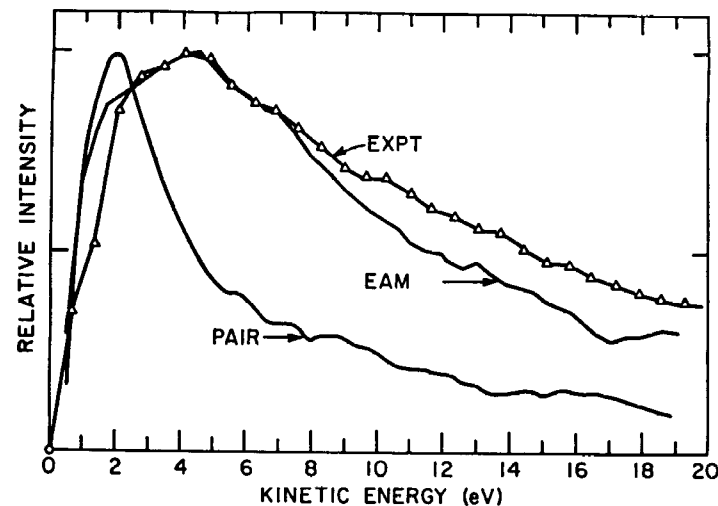


Fig. 6. Experimental and calculated angle-integrated kinetic energy distributions. In all cases the curves are peak normalized. (Modified from Ref. 9.)

As shown in Fig. 4, molecular dynamics calculations using pairwise-additive potentials do quite well at reproducing and explaining the angular distributions of Rh atoms ejected from Rh(111). The question is then, are many-body potentials necessary or is the ejection process dominated by crystal structure and thus the repulsive wall of the potential? Shown in Fig. 6 are measured and calculated (with pairwise-additive potentials) angle-integrated energy distributions⁹. The curves do not agree nor could they be made to agree with any reasonable variation of the parameters. In addition, the calculated peaks in the polar distributions (Fig. 4) were $5-10^\circ$ closer to the surface normal than the experimental ones.

A preliminary fit of the embedding function and the core repulsive term was made to the properties of Rh metal in order to determine if the EAM description of the interaction better predicts the EARN data of Rh atoms ejected from Rh(111) than the pair potentials⁹. The most dramatic change in the predicted distributions arises in the angle-integrated energy distributions. As shown in Fig. 6 the experimental and calculated distributions using the EAM interaction are in excellent agreement while the calculated distribution using pair potentials is quite different from the experimental curve. The peak in

the polar angle distributions as calculated from the EAM are also found to increase by about 10° from those predicted by the pair potentials (Fig. 4). The agreement between the EAM and the experimental energy distributions is better than one could have hoped, and the polar distribution correction is in the right direction.

Is the better agreement fortuitous or is there a sound basis for it? The pair-potential description in the surface region has been thought to be inadequate but the detailed data that exposed the nature of the deficiencies was not available. There are several differences between the EAM and pair potentials. First the surface binding energy of the EAM potential is larger (5.1 eV) than that of the pair potential (4.1 eV). Of note is that both potentials were fit to the bulk heat of atomization of Rh (5.76 eV). The peak position in the energy distribution is proportional to the binding energy¹³⁵, thus it is logical that the peak in the EAM energy distribution occurs at a higher value than for the pair potential. In addition to the larger binding energy at the equilibrium site, the EAM potential is relatively flat in the attractive portion of the entire surface region. There is more than a 4 eV attraction for the ejecting atom even above a neighboring atom, while the pair potential has only ~ 1 eV overall attraction. Thus particles that eject at more grazing angles will experience a larger attraction to the surface in the EAM potential than in the pair potential. This will tend to make the peak in the energy distribution shift to larger energies, and will also pull the particles away from the surface normal and move the peak in the polar distribution (Fig. 4).

Recently the previously developed Rh(111) EAM potential has been employed to model the ejection process from Rh(331), a stepped surface that consists of (111) terraces three atoms wide with a one-atom step height. In this surface there are atoms that are both more and less coordinated than on the (111) surface. The agreement between the experimental and calculated angular distributions is excellent¹³⁶. This same EAM potential was used for the Rh interactions in the O/Rh(111) study discussed in section 2.

In a similar study, Lo *et al.* have compared the characteristics of atoms sputtered from copper surfaces in simulations which used both pair-additive potentials and EAM potentials¹³⁷. Significant differences were found for many properties of interest, including the peak in the energy distributions. Although adjustment of the potentials to fit experimental data was not attempted, this study concluded that many-body potentials are required to realistically model much of the sputtering process.

The EAM approach appears to provide a formalism within which realistic potentials which describe atomic dynamics can be developed. It should also provide a method for realistically incorporating adsorbates into dynamics simulations. Both of these applications can be considered significant advances, and will help molecular dynamics simulations to continue to contribute to the understanding of technologically important processes.

3.3. Silicon: covalent many-body potentials

There has been recent widespread interest in simulating semiconductors. This has been especially true for silicon, and to a lesser extent for germanium. Prior to 1984, no general potential energy expressions were available which could be used to model the chemical dynamics of semiconductors. Between 1984 and 1986, at least five different expressions were introduced which can successfully model condensed phases of silicon^{34,37,39,41,46}. These potential energy schemes, which were discussed in section 1.2, have made possible the use of molecular dynamics to study atomic-scale motion on semiconductor surfaces.

Reactions that occur on the surface of covalent solids have a complexity that is not as prevalent in metals. Many metal surfaces, especially the close-packed faces, retain the same geometry and bonding arrangement as would be present in the bulk phase. Most semiconductor surfaces, however, undergo reconstructions in which the surface atoms move significant distances from the bulk terminated positions. For example, the Si(001) surface, if bulk terminated, would have each atom bonded to two other silicon atoms in the second layer (Fig. 7). There would be two dangling bonds each with one electron, and the

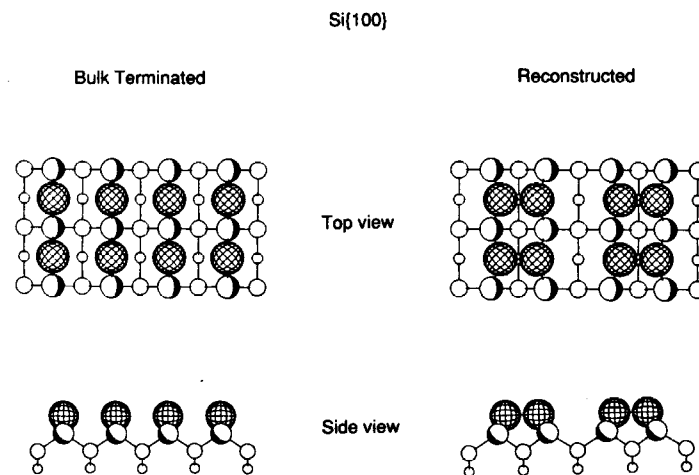


Fig. 7. Si(001). Bulk terminated atom positions, top and side views. (2×1) dimer reconstruction, top and side views. In all cases, the first-layer atoms are hatched, the second-layer atoms are shaded and deeper-layer atoms are smaller. (Drawn by Tracy Schoolcraft.)

nearest-neighbor distance on the surface would be $\sim 3.84 \text{ \AA}$. Since Si prefers higher coordination environments two surface atoms react and form a bond (i.e. 'dimerize') – with a distance of $\sim 2.4 \text{ \AA}$ (Fig. 7)^{138–146}. The Si(111) surface reconstructs with a unit cell 7 times that of the bulk terminated surface with a reconstruction thought to involve vacancies, adatoms and five and seven-membered rings^{146–152}. If one is going to realistically model reactions on these surfaces, then the reconstructions must be incorporated into the simulation.

Two popular means of growing silicon single crystals are molecular beam epitaxy (MBE) and chemical vapor deposition (CVD)^{153–156}. In MBE a beam of Si atoms from an oven source impinges on a Si crystal surface with the goal being to grow additional crystalline layers. Since the timescale of this process is approximately a layer per minute, there is ample time for diffusion of adsorbed atoms, reactions to remove surface reconstructions, and growth of subsequent layers. In CVD a gas of silanes (SiH_4 , Si_2H_6) is present above the Si crystal surface and reactions occur between the gas and surface which result in the growth of a single crystal. Again numerous processes including diffusion, removal of the reconstruction, and crystal growth can and do occur.

3.3.1. Silicon on silicon

As described above, silicon crystals can be grown from a variety of gas sources. Because the rate of growth can be modulated using these techniques, dopants can be efficiently incorporated into a growing crystal. This results in control of the atomic structure of the crystal, and allows the production of samples which have specific electronic properties. The mechanisms by which gas-phase silicon species are incorporated into the crystal, however, are still unclear, and so molecular dynamics simulations have been used to help understand these microscopic reaction events.

(a) Surface diffusion

The growth rate of silicon crystals by either MBE or CVD is relatively slow, and so there is ample time for adsorbed atoms and molecules to diffuse to energetically more favorable sites. Experimental rates of diffusion of silicon on silicon and the activation barriers, however, are not known well. Experimental estimates of the activation barrier for silicon atoms diffusing on the Si(111) surface have ranged from 58 kcal/mole when the pyrolysis of silane is used to produce surface silicon atoms¹⁵⁷, to 4.6 kcal/mole for the direct deposition of silicon atoms under ultrahigh vacuum¹⁵⁸. Furthermore, a comparison of these values with other silicon crystal faces has not been available. Because data for surface diffusion is necessary to model various aspects of semiconductor production, there has been interest in using molecular dynamics as a method of confirming and characterizing experimental observations.

In an effort to understand silicon surface diffusion, NoorBatcha, Raff and Thompson have employed molecular dynamics to model the motion of single silicon atoms on the Si(001) and Si(111) surfaces¹⁵⁹. Morse functions are used for the pair forces, with the parameters being determined by the heat of sublimation. Because different forces were used for the diffusing and substrate atoms, the incorporation of gas-phase species into the crystal could not be directly modeled. Nonetheless, they were able to explore the characteristics of adsorption and diffusion for single atoms.

Using classical trajectories, NoorBatcha *et al.* determined a sticking coefficient of 0.96 for adsorption of Si atoms on the (001) surface¹⁵⁹, and effective activation energies of 3.63 kcal/mole and 2.43 kcal/mole for diffusion on the Si(001) and Si(111) surfaces, respectively^{159,160}. The calculated sticking coefficient is in agreement with the experimentally determined value of near unity¹⁶², and the activation energies suggest that the experimental number of 4.6 kcal/mole for diffusion on the (111) surface is the more accurate value. They also found diffusion on the Si(001) surface to be highly anisotropic, with atoms diffusing along channels in the surface. Similar modes of anisotropic diffusion have been proposed as being responsible for the occurrence of steps with specific orientations during the deposition of silicon atoms on the Si(001) surface¹⁶³.

In a subsequent study, NoorBatcha *et al.* varied the valence-force parameters used for the lattice interactions to evaluate the effect of the vibrational properties of the crystal on diffusion characteristics¹⁶¹. Using three sets of lattice potential parameters, they determined a range of effective activation barriers for diffusion of 3.63 kcal/mole to 7.47 kcal/mole on the Si(001) surface. This range encompasses the experimental estimate of 4.6 kcal/mole for the Si(111) surface, and further suggests this value as the more accurate experimental estimate.

In a similar study, Khor and Das Sarma studied the diffusion of Si, Si₂ and Si₃ on the (001), (011), and (111) surfaces of silicon¹⁶⁴. In their study, the forces on all of the atoms were determined by the Stillinger–Weber potential³⁴. For single atoms on all surfaces, they report an upper bound for diffusion of $4.8 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 1600 K. This value is significantly less than both the range determined by NoorBatcha of 2.031×10^{-4} to $15.8 \times 10^{-4} \text{ cm}^2/\text{sec}$ ^{159–161}, and the experimental estimate of $\sim 10^{-3} \text{ cm}^2/\text{sec}$ ¹⁵⁸. They also report that diatomic Si₂ molecules diffuse more readily than single atoms on the Si(111) surface.

Despite the insights which the dynamics have provided into surface diffusion, additional studies will be required to fully characterize surface dynamics. In particular, the role of surface reconstructions on diffusion has not been fully explored, and additional studies of the relationship between anisotropic diffusion and step stability are currently needed.

(b) Epitaxial growth

Another area in which molecular dynamics has been used is in the study of the dynamics and structure of vapor-deposited crystals¹⁶⁵⁻¹⁶⁷. The main drawback to using molecular dynamics to study vapor-phase deposition is that epitaxial growth is an intrinsically slow process. Typical growth rates for techniques which employ molecular beams are on the order of monolayers per minute, while present timescales accessible to molecular dynamics stretch from picoseconds to nanoseconds. In a recent article by Abraham, the amount of CPU time on a Cray supercomputer required to simulate modest realistic growth conditions using a Lennard-Jones potential is estimated to be seven months⁴. If one of the silicon potentials currently available were substituted for the pair-additive interactions, this estimate would increase dramatically. Nonetheless, it is expected that dynamics simulations can provide important microscopic information about the growth process, and so studies of silicon growth at high deposition rates have been undertaken.

Gossmann and Feldman have employed a combination of low-energy electron diffraction (LEED) and high-energy ion scattering to experimentally probe the structure of the (001) and (111) surface of silicon during the deposition of silicon atoms¹⁶⁸. This combination of experimental techniques provides a very good characterization of surface structures. This is because LEED probes the long-range symmetry of the first few atomic layers, while ion scattering provides information on the short-range structure of all atomic layers which are displaced from bulk positions¹⁶⁹. In their studies, molecular beams were used to deposit controlled amounts of silicon atoms on substrates which were maintained at various constant temperatures. This allowed intermittent determinations of surface structures during the growth process.

As discussed above, the Si(001) surface is reconstructed into dimers, a side view of which is shown in Fig. 7. In addition to the reconstruction of the surface atoms there is significant distortion of the subsurface region. This distortion blocks channels which enter into the bulk, and causes an excess of backscattered ions over what would be expected from atomic rows in the ideal crystal. This local distortion is the property monitored by backscattered ion intensities. The dimer pairs also tend to form in rows, which is the source of the (2×1) LEED pattern observed for this surface.

For the deposition of silicon on Si(001) and Si(111) surfaces, Gossmann and Feldman determined that epitaxial growth occurs for substrate temperatures maintained over 570 K and 640 K, respectively¹⁶⁸. Above the epitaxial temperature the growth is single crystal, while below this temperature the growth is amorphous. This difference in epitaxial growth temperature between the two faces was ascribed by Gossmann and Feldman to be due to the different surface reconstructions, where the (111) surface presumably

requires a higher temperature to 'unreconstruct' during deposition than the (001) surface. They also observed that for the deposition of up to ~ 3 monolayers on the (001) surface at low temperatures, the (2×1) symmetry of the surface was lost, yet the number of backscattered ions remained constant. This is in contrast to epitaxial growth at high substrate temperatures, where both sharp diffraction patterns and constant ion-scattering signals were reported for all coverages. Furthermore, as additional monolayers were deposited, the number of backscattered ions increased and the surface symmetry changed to (1×1) , i.e. the same as the bulk terminated surface.

Gossmann and Feldman proposed that the initially constant backscattered ion intensities were a result of two effects. First, as the silicon was being deposited, channels into the lattice were being filled. This would result in an increased number of backscattered ions. At the same time, however, they proposed that the reconstruction was being disordered, and so the channels which were originally blocked by the subsurface distortion were opening. This would result in a decreasing number of backscattered ions. The net result of these two effects would be an almost constant backscattered-ion intensity. Furthermore, because approximately three surface layers were distorted due to the reconstruction, this cancellation would occur for the deposition of approximately three monolayers, as observed experimentally. The conclusions of the study were that for high substrate temperatures (above 560 K), epitaxial growth occurred. For low substrate temperatures, however, deposited atoms form amorphous or polycrystalline layers, with the ion-scattering results suggesting that these layers reorder the initial reconstruction.

Two molecular dynamics studies of the gas-phase deposition of silicon atoms on the silicon (001) reconstructed surface have been reported. In a pair of simulations which used the Stillinger-Weber potential³⁴, Gawlinski and Gunton modeled the gas-phase growth of silicon by depositing eight monolayers of silicon atoms on reconstructed (001) substrates¹⁶⁵. In one simulation, the substrate was maintained at a low temperature of 250 K, while in the other the substrate was maintained at a high temperature of 1500 K. These two temperatures were chosen because they are below and above the epitaxial growth temperature reported by Gossmann and Feldman. After the low-temperature deposition, they observed that the surface of the initial substrate (which was buried under the deposited atoms) remained relatively unchanged, while for deposition on the high-temperature substrate the initial surface reconstruction was disordered. Furthermore, they observed that for the low-temperature deposition, amorphous overlayers resulted, while for deposition on the higher-temperature substrate enhanced ordering of the surface layers was apparent. Despite the very high deposition rate used in this study, the difference between the structures produced at the two growth

temperatures reflected a difference in growth modes as suggested by Gossmann and Feldman's study. This result also confirmed the idea that molecular dynamics can be successfully used to study crystal growth.

In a different approach to this problem, Brenner and Garrison used molecular dynamics to examine the chemical mechanisms which lead to reordering of the atom-pairing reconstruction during atom deposition¹⁶⁶. This simulation incorporated a dissociative valence-force field potential³⁹ and consisted essentially of a high-temperature anneal of $1\frac{1}{2}$ monolayers of silicon atoms which had been deposited on a silicon (001) reconstructed surface.

During the dynamics, two modes of surface dimer opening ('unreconstruction') were observed. In the first mode the distance between the two atoms in a dimer pair would intermittently change between that corresponding to the reconstruction, and the distance corresponding to the bulk terminated surface. This mechanism, termed an unstable opening, resulted when a surface dimer was surrounded by several randomly positioned atoms. Because the atoms surrounding the open dimer were not in lattice sites, this mode of dimer opening was proposed as being the initiation of an amorphous overlayer which reorders the reconstruction. Also, since diffusion did not play a large role, this was associated with the low-temperature growth mode proposed by Gossmann and Feldman.

The second dimer-opening mode observed resulted when a surface atom diffused to the site of a surface dimer and 'bumped' a nearby atom into the center of the dimer. This mechanism resulted in atoms which occupied lattice sites, and produced a surface dimer which remained open for the course of the simulation. Because the final atomic positions corresponded to lattice sites, and because a high rate of surface diffusion was required to produce the 'bump', this mechanism was associated with the high-temperature epitaxial growth mode identified by Gossmann and Feldman.

A related area of crystal growth for which the short timescale required by molecular dynamics is more appropriate is kinetic-energy-enhanced epitaxial growth. In this technique, an energized beam is used to deposit atoms on a surface. For silicon beam deposition of energies 10–65 eV, epitaxial growth has been reported for colder substrate temperatures than is required when thermal beams are used¹⁷⁰. For energies above about 100 eV, however, enhanced damage of up to 400 Å below the surface has been reported. Based on these experimental observations, there appears to be a limited range of energies which are of use for producing good-quality films. Molecular dynamics simulations have been used to better quantify damage caused by the energetic beam, and to suggest extensions to this technique.

Dodson has used molecular dynamics to study atom-surface dynamics for silicon atom energies ranging from 10 to 100 eV incident on a silicon (111) surface¹⁷¹. In this study a modified form of the Tersoff potential was

employed⁴⁵, and substrates of various sizes were used. For an energy of 10 eV and near-perpendicular angles of incidence, 30% of the deposited atoms were reported to come to rest on the top of the substrate, and the remaining 70% penetrated into subsurface interstitial sites. If the angle of incidence was changed to 60°, however, roughly half of the atoms were reported to have remained on the surface. Dodson's simulations also indicate that kinetic energy transfer between the incoming atoms and the lattice is rapid, with a majority of the initial kinetic energy of the atom being dissipated by phonons within about 0.08 ps.

Dodson also explored the motion of silicon atoms with kinetic energies in the range 20–100 eV that were initially incident on the surface with near grazing angles. In these trajectories the incoming atoms were observed to skip along the surface, traveling with ranges of up to thousands of angstroms. This observation suggests that energized beams could be used to greatly increase surface diffusion, and thereby produce an efficient mode of transporting atoms to steps or defects. This could result in better-quality films, and could offer promise for effectively controlling growth structures.

In another molecular dynamics study, Garrison, Miller and Brenner characterized the chemical dynamics of silicon atoms with energies of 0.026–20 eV which were deposited on a silicon (001) dimer-reconstructed surface¹⁷². For atomic energies of 0.026 eV and perpendicular incidence, the atoms in the beam remained on the surface, and no significant motion of the dimer-reconstructed surface atoms occurred. For energies in the range of 5–10 eV, however, significant motion of the surface atoms was observed which led to epitaxial atomic configurations. One mechanism which occurred in this energy range was the direct insertion of the incoming atom into the dimerized pair of surface atoms (Fig. 8). In a second mechanism, the incoming atom replaced one of the atoms in a surface dimer pair, which then became the inserted atom. Finally, the incoming atom could also knock open the dimer, and bind to the surface so that the dimer remained open. Each of these mechanisms took place on a timescale of ~100 fs, and so they are best characterized as direct dimer-opening processes. This is opposed to a thermal process where many vibrations might be required. Although not all trajectories in this energy range produced open dimer pairs, the results of the simulation indicate that the energy range of up to 10 eV would enhance epitaxial growth without introducing subsurface defects.

In addition to the 5–10 eV energy range, incoming atoms with energies of up to 20 eV were also explored. These atoms were observed to implant into the lattice, and presumably produce damage in a growing film. This conclusion agrees with that of Dodson, where a majority of atoms incident perpendicular to the (111) with energies of 10 eV implanted. These studies indicate that for perpendicular incidence, atoms with energies in the range 5–10 eV would be the most effective for producing low-temperature epitaxial films.

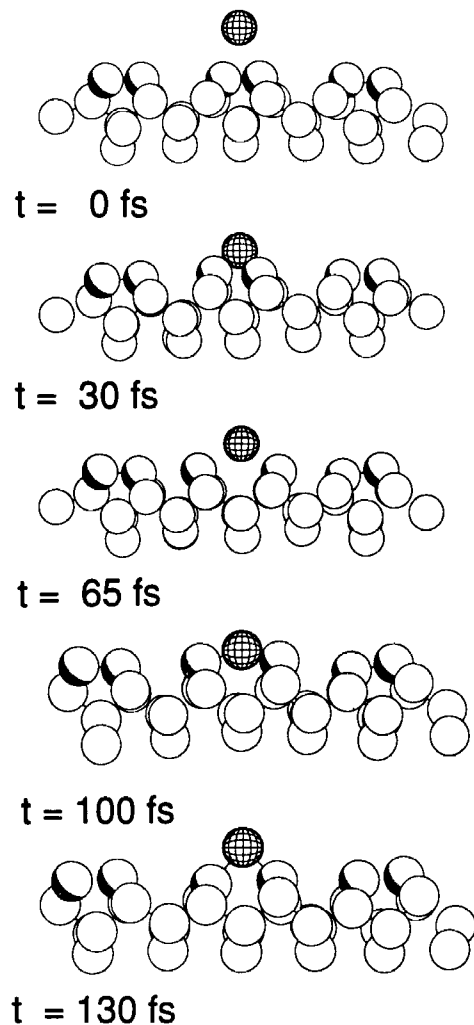


Fig. 8. Insertion mechanism of dimer opening as a function of time in femtoseconds (fs). The adatom started with 7.5 eV of kinetic energy and oriented perpendicular to the surface. The hatched circles represent the adatoms, the shaded circles the original surface dimer atoms and the open circles the substrate atoms. Only four layers of the ten used in the simulation are shown. (From Ref. 172.)

3.3.2. Hydrogen on silicon

Despite the potential for atomic-scale manipulation of interfaces displayed by molecular-beam epitaxial growth, a majority of the vapor-phase growth of silicon is accomplished by the reaction of silane with silicon substrates¹⁵³. This is because much higher growth rates can be achieved, and because silane is readily available. The presence of hydrogen in the reacting species, however, increases the complexity of the problem, and makes this a much more difficult system to study theoretically. Relatively few molecular dynamics simulations of the reaction of hydrogen atoms on silicon substrates have therefore been reported.

Raff, Thompson and coworkers have carried out a series of studies which have examined the reaction dynamics of hydrogen atoms and molecules with silicon substrates^{173,174}. Rice *et al.* used a variation of the NoorBatcha silicon-on-silicon model described above to simulate the scattering and dissociative sticking of H_2 on the Si(111) surface¹⁷⁴. The potential used was a valence-force field expression for the atoms in the substrate, and a sum of pairwise-additive Morse functions for the interactions between the hydrogen atoms and the substrate. The parameters used in the Morse functions were determined by the isolated H_2 molecule, and by fitting to various H_2 -silicon cluster calculations¹⁷³. Rice *et al.* determined that for H_2 molecules striking the surface with energies less than the barrier for dissociative adsorption (0.18 eV for their potential), scattering was elastic and predominately specular. They also found very little rotational or vibrational energy transfer between the H_2 molecules and the surface.

For the interaction of H_2 with energies greater than 0.18 eV, Rice *et al.* reported that all cases of H_2 adsorption were accompanied by dissociation of the molecule. This is in agreement with experimental observation, where the chemisorption of intact H_2 molecules has not been reported¹⁷⁵. Furthermore, for all cases they report that both H atoms chemisorb to the surface rather than reflect back into the gas phase. The dissociative adsorption of H_2 was accompanied by an energy release of between 2.5 and 4.3 eV. The energy released was shown to enhance the initial mobility of the H atoms on the surface, and was reported to be somewhat independent of the surface temperature. Once the energy was dissipated to the surface, however, the mobility of the H atoms decreased sharply.

In a subsequent study, Agrawal, Raff and Thompson showed that the sticking probability for the H_2 molecule was independent of the interactions used for the substrate atoms⁴⁰. The mobility of the H atoms and the rate of energy transfer between the H atoms and the substrate, however, were reported to depend somewhat on the lattice. Despite the small dependence on the substrate model, the major results of the initial study remained unchanged.

The reaction of silane in the gas phase and with silicon surfaces is a complex

topic to understand on an atomic scale. The molecular dynamics studies described above, however, have shed light on the rates and mechanisms of various reactions involved. Further studies along these lines will undoubtedly prove valuable to understanding the details of this process.

4. THE FUTURE OF MOLECULAR DYNAMICS FOR MODELING GAS-SURFACE REACTIONS

The past few years have been an exciting time for modeling gas-surface reactions. Computational techniques as well as potential energy functions have become sufficiently advanced that dynamics simulations can now describe many realistic situations without introducing severe approximations. As computer resources continue to grow, the impact which computer modeling has on science and engineering will also continue to increase.

Significant progress has recently been made in several areas which will have a profound effect on the ability of molecular dynamics to handle more complex problems. In this section we speculate on several areas which appear to hold promise for advancing computer modeling studies. In section 4.1, recent progress in both analytic potential energy expressions and 'first principles' calculations are briefly mentioned. Recent advances in computational techniques are discussed in section 4.2. These include the use of constraints within the classical equations of motion to model thermostats in the surface region, and the incorporation of Monte Carlo techniques into molecular dynamics simulations.

4.1. Further development of potential-energy expressions

A great deal of recent success has been achieved in writing simple analytic potential energy expressions which capture the essence of chemical bonding. Much of the inspiration for these efforts has come from the desire to realistically model reactions in condensed phases and at surfaces. As computer simulations grow in importance, continued progress in the development of new potential energy functions will be needed.

In the near future, the expansion of the covalent-bonding formalisms developed to model silicon to other systems appears promising. Very recently the extension of the Abell-Tersoff covalent-bonding formalism to few-body reactive systems has been demonstrated by the development of an accurate potential energy expression for H_3 ¹⁷⁶. In the determination of an analytic potential function for silicon, Tersoff's main objective was to describe the energetics of stationary points on the potential surface^{41,42}. This emphasis did not include properties of importance to chemical dynamics such as potential barriers, and so it was not clear if this formalism could be used to describe

chemical reactions. In the H_3 study, the potential energy for different atomic configurations which had been calculated by *ab initio* methods were accurately fitted using a Tersoff-type expression. This demonstrated that potential barriers to reaction can be introduced within this formalism, and that it is sufficiently flexible to accurately describe few-body potential energy surfaces.

The Abell-Tersoff potential energy expression has also been used to describe reactive collisions in molecular solids¹⁷⁷. These studies have modeled detonation and energetic-ion induced chemistry, and have demonstrated that the energetics of propagating reactions in solids can be understood using models derived from gas-phase reactivity¹⁷⁸. The application of this approach to these systems suggests that this formalism will be useful for modeling molecule-surface reactions where the dynamics of both substrate atoms and arrays of molecules are of importance. For example, the incorporation SiH_4 molecules into a silicon substrate could possibly be modeled using this formalism. Such studies could be thought of as incorporating the advantages of simulations which use LEPS potentials, such as adjustable potential energy barriers, with the ability to describe covalent bonding in solids.

In a similar fashion, the introduction of angle-dependent electron densities into the EAM³³ suggests that this formalism may be successfully extended to chemical reactions. This would allow the study, for example, of the reaction of a metal-ligand cluster with a metal surface. This would enhance the applicability of the EAM, and would increase the realm of processes which computer simulations can effectively model.

In addition to analytic potential energy expressions, studies have begun which introduce forces calculated from *ab initio* total energy techniques directly into dynamics simulations. One method which has attracted considerable attention is based on the concept of simulated annealing¹⁷⁹. Car and Parrinello originally introduced this technique as a way of unifying density-functional theory and molecular dynamics¹⁸⁰. The idea is that the (classical) nuclear degrees of freedom and the electronic degrees of freedom (which enter through a variational wavefunction) are varied simultaneously. The approach taken is to treat the parameters which enter the wavefunction as classical 'particles', and to write equations of motion for each of the parameters. The forces on the atoms are derived from the electronic wavefunction, while the forces on the wavefunction 'particles' are determined by the condition that the electronic energy be minimized subject to the relative positions of the nuclei. By integrating the electronic degrees of freedom simultaneously with the nuclear degrees of freedom, the minimum energy state of the system can be determined with a smaller amount of effort than would be required if both were minimized separately. Examples where variations of this method have been applied include the calculation of the structure and energetics of various silicon¹⁸⁰⁻¹⁸², germanium¹⁸³⁻¹⁸⁵ and silicon oxide compounds¹⁸⁶, and the

optimization of basis sets for diatomic molecules¹⁸⁷ and solvated electrons^{188,189}.

The major drawback for employing the Car-Parrinello approach in dynamics simulations is that since a variational wavefunction is required, the electronic energy should in principle be minimized before the forces on the atoms are calculated. This greatly increases the amount of computer time required at each step of the simulation. Furthermore, the energies calculated with the electronic structure methods currently used in this approach are not exceptionally accurate. For example, it is well established that potential energy barriers, which are of importance to chemical reactivity, often require sophisticated methods to be accurately determined. Nonetheless, the 'first-principles' calculation of the forces during the dynamics is an appealing idea, and will continue to be developed as computer resources expand.

A second marriage between electronic structure techniques and molecular dynamics simulation has been the calculation of atomic forces using semiempirical tight-binding electronic structure methods¹⁹⁰⁻¹⁹². Menon and Allen, for example, have used this method to model the dynamics of a gas-phase atom interacting with a semiconductor surface¹⁹¹. While simulations of this type have proven to be feasible, again finite computer resources restrict the size and length of time of the processes which can be modeled. Also, the energetics calculated by tight-binding methods are not exceptionally accurate for properties such as barriers to reaction, and so the dynamics generated in this way may not always be physically significant.

4.2. Advances in dynamics techniques

In addition to the study of atomic motion during chemical reactions, the molecular dynamics technique has been widely used to study the classical statistical mechanics of well-defined systems. Within this application considerable progress has been made in introducing constraints into the equations of motion so that a variety of ensembles may be studied². For example, classical equations of motion generate constant energy trajectories. By adding additional terms to the forces which arise from properties of the system such as the pressure and temperature, other constants of motion have been introduced.

The addition of constraints to the equations of motion have also been used to produce thermostats at surfaces which control the flux of heat in and out of the substrate. For example, Riley *et al.* have proposed a velocity reset procedure which regulates atomic motion by coupling the current velocity of each atom with a velocity chosen from a Maxwellian distribution¹⁹³. In a similar scheme, Agrawal *et al.* have added a friction term to atomic velocities which depends in part on the difference between the current temperature of the surface region and that desired for the substrate⁴⁰. This approach was

originally proposed by Berendsen *et al.* as an alternative to the generalized Langevin equation for bulk phases¹⁹⁴, and it can apparently be applied to surface dynamics. Other similar constrained dynamics schemes, which have arisen from simulations of bulk materials, will also play a role in the dynamics of surface reactions.

One final area which will increase the flexibility of molecular dynamics simulations is the incorporation of Monte Carlo techniques. Because molecular dynamics follows atomic motion in real time, it can be used to study nonequilibrium as well as equilibrium dynamics. Molecular dynamics time-scales, however, are currently limited to about the nanosecond range, and so it cannot be used to model processes which require long times. For example, surface diffusion at room temperature often consists of jumps between lattice sites. The time spent at each lattice site, however, can be long compared to the time required to complete a jump, and so the observation of a sufficient number of jumps to estimate surface diffusion properties can require an enormous amount of computer time. In contrast to molecular dynamics, the Monte Carlo technique involves moving atoms in a random fashion with the acceptance of moves depending on the potential energy and a predetermined temperature¹⁹⁵. The main advantage of the Monte Carlo technique over molecular dynamics is that the configurations sampled by the moves can be restricted to those which are of direct interest to the process being modeled. For example, in the case of surface diffusion the position of the diffusing species may be restricted to regions near lattice sites and saddle points¹⁹⁶⁻¹⁹⁸. This approach, in conjunction with techniques such as transition-state theory, can lead to accurate estimates of surface diffusion without the need to perform extensive dynamics calculations between jumps.

A marriage between Monte Carlo techniques and molecular dynamics simulations can be envisioned for situations where both short-time nonequilibrium dynamics and long-time equilibrium processes are important. For example, the growth of silicon from silane involves the dissociative chemisorption of molecules on the surface, as well as the long-time diffusion of surface species. If the reactions are studied with molecular dynamics, and surface diffusion is included using Monte Carlo techniques, then a complete picture of the dynamics of growth can in principle be obtained. Although few studies of this type have been undertaken, we believe that such techniques will ultimately prove very useful for modeling technologically important processes.

In this article we have tried to present a general, although somewhat limited overview of molecular dynamics simulations of gas-surface reactions as they pertain to technologically important processes. In the course of this review we have undoubtedly left out a great deal of very important work. We hope,

however, that the prospect for significant advances in this area has been conveyed, and that the continued success of these types of studies is apparent.

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References

- Gay, W. L., and Harrison, D. E., Jr., *Phys. Rev.*, **135**, A1780 (1964); Harrison, D. E., Jr., Johnson, J. P. III, and Effron, H. M., *Appl. Phys. Lett.*, **8**, 33 (1966); Harrison, D. E. Jr., and Delaplain, C. B., *J. Appl. Phys.*, **47**, 2252 (1976); Harrison, D. E. Jr., *CRC Critical Reviews in Solid State and Materials Sciences*, **14**, S1 (1988); Garrison, B. J., and Winograd, N., *Science*, **216**, 805 (1982).
- Hoover, W. G., *Molecular Dynamics*, Springer-Verlag, Berlin, 1986.
- Heerman, D. W., *Computer Simulation Methods in Theoretical Physics*, Springer-Verlag, Berlin, 1986.
- Abraham, F. F., *Adv. Phys.*, **35**, 1 (1986).
- Fincham, D., and Heyes, D. M., *Adv. Chem. Phys.*, **63**, 493 (1985).
- Klein, M. L., *Ann. Rev. Phys. Chem.*, **36**, 525 (1985).
- Hockney, R., and Eastwood, J., *Computer Simulations using Particles*, McGraw-Hill, New York, 1981.
- Hafner, J., and Heine, V., *J. Phys. F: Met. Phys.*, **13**, 2479 (1983).
- Garrison, B. J., Winograd, N., Deaven, D. M., Reimann, C. T., Lo, D. Y., Tombrello, T. A., Harrison, D. E., and Shapiro, M. H., *Phys. Rev. B*, **37**, 7197 (1988).

- Torrens, I. M., *Interatomic Potentials*, Academic Press, New York, 1972.
- Bohr, N., *Kgl. Dansk. Vid. Selsk. Mat.-Fys. Medd.*, **18**, No. 8 (1948).
- Born, M., and Mayer, J. E., *Z. Phys.*, **75**, 1 (1932).
- Daw, M. S., and Baskes, M. I., *Phys. Rev. B*, **29**, 6443 (1984).
- Daw, M. S., *Surf. Sci.*, **166**, L161 (1986).
- Ercolessi, F., Tosatti, E., and Parrinello, M., *Phys. Rev. Lett.*, **57**, 719 (1986).
- Ercolessi, F., Parrinello, M., and Tosatti, E., *Surf. Sci.*, **177**, 314 (1986).
- Garofalo, M., Tosatti, E., and Ercolessi, F., *Surf. Sci.*, **188**, 321 (1987).
- Tomanek, D., and Bennemann, K. H., *Surf. Sci.*, **163**, 503 (1985).
- Dodson, B. W., *Phys. Rev. B*, **35**, 880 (1987).
- Chen, S. P., Voter, A. F., and Srolovitz, D. J., *Phys. Rev. Lett.*, **57**, 1308 (1986).
- Sathyamurthy, N., *Computer Phys. Reports*, **3**, 1 (1985), and references therein.
- Murrell, J. N., Carter, S., Farantos, S. C., Huxley, P., and Varandas, A. J. C., *Molecular Potential Energy Functions* Wiley, New York, 1984, and references therein.
- McCreery, J. H., and Wolken, G., *J. Chem. Phys.*, **63**, 2340 (1975).
- McCreery, J. H., and Wolken, G., *J. Chem. Phys.*, **67**, 2551 (1977).
- Wolken, G., and McCreery, J. H., *Chem. Phys. Lett.*, **54**, 35 (1978).
- Wolken, G., *J. Chem. Phys.*, **68**, 4338 (1978).
- Purvis, G. D., and Wolken, G., *Chem. Phys. Lett.*, **62**, 42 (1979).
- Barnett, R. N., Cleveland, C. L., and Landman, U., *Phys. Rev. Lett.*, **54**, 1679 (1985).
- Foiles, S. M., Baskes, M. I., and Daw, M. S., *Phys. Rev. B*, **33**, 7983 (1986).
- Foiles, S. M., *Phys. Rev. B*, **32**, 7685 (1986).
- Felter, T. E., Foiles, S. M., Daw, M. S., and Stulen, R. H., *Surf. Sci.*, **171**, L379 (1986).
- Deaven, D. M., Honors Thesis, The Pennsylvania State University, 1988.
- Baskes, M. I., *Phys. Rev. Lett.*, **59**, 2666 (1987).
- Stillinger, F. H., and Weber, T. A., *Phys. Rev. B*, **31**, 5262 (1985).
- Khor, K. E., and Das Sarma, S., *Phys. Rev. B*, **36**, 7733 (1987).
- Abraham, F. F., and Batra, I. P., *Surf. Sci.*, **163**, L752 (1985).
- Pearson, E., Takai, T., Halicioglu, T., and Tiller, W. A., *J. Crystal Growth*, **70**, 33 (1984).
- Axilrod, B. M., and Teller, E., *J. Chem. Phys.*, **11**, 299 (1943).
- Brenner, D. W., and Garrison, B. J., *Phys. Rev. B*, **34**, 1304 (1986).
- Agrawal, P. M., Raff, L. M., and Thompson, D. L., *Surf. Sci.*, **188**, 402 (1987).
- Tersoff, J., *Phys. Rev. Lett.*, **56**, 632 (1986).
- Tersoff, J., *Phys. Rev. B*, **37**, 6991 (1988).
- Abell, G. C., *Phys. Rev. B*, **31**, 6184 (1985).
- Brenner, D. W., Ph.D. Thesis, The Pennsylvania State University, 1987.
- Dodson, B. W., *Phys. Rev. B*, **35**, 2795 (1987).
- Biswas, R., and Hamann, D. R., *Phys. Rev. Lett.*, **55**, 2001 (1985).
- Khor, K. E., and Das Sarma, S., *Chem. Phys. Lett.*, **134**, 43 (1987).
- Ding, K., and Anderson, H. C., *Phys. Rev. B*, **34**, 6987 (1986).
- Grabow, M. H., and Gilmer, G. H., in *initial Stages of Epitaxial Growth* (Eds. J. M. Gibson, R. Hull and D. A. Smith), Materials Research Society, Pittsburgh, 1987, p. 15.
- Fitz, D. E., Bowagan, A. O., Beard, L. H., Kouri, D. J., and Gerber, R. B., *Chem. Phys. Lett.*, **80**, 537 (1981).
- Barker, J. A., Kleyn, A. W., and Auerbach, D. J., *Chem. Phys. Lett.*, **97**, 9 (1983).
- Polanyi, J. C., and Wolf, R. J., *J. Chem. Phys.*, **82**, 1555 (1985).

53. Muhlhausen, C. W., Williams, L. H., and Tully, J. C., *J. Chem. Phys.*, **83**, 2594 (1985).
54. Certain, P. R., and Bruch, L. W., in *Physical Chemistry*, Series One, Vol. I (Ed. W. B. Brown), University Park Press, Baltimore, 1972.
55. Fitts, D. D., *Ann. Rev. Phys. Chem.*, **17**, 59 (1966).
56. Benninghoven, A., Jaspers, D., and Sichterman, W., *Appl. Phys.*, **11**, 35 (1976).
57. Baxter, J. P., Schick, G. A., Singh, J., Kobrin, P. H., and Winograd, N., *J. Vac. Sci. Technol.*, **4**, 1218 (1986).
58. Schick, G. A., Baxter, J. P., Singh, J., Kobrin, P. H., and Winograd, N., in *Secondary Ion Mass Spectrometry-SIMS V*, Vol. 44 of Springer Series in Chemical Physics (Eds A. Benninghoven, R. J. Colton, D. S. Simons, and H. W. Werner), Springer, New York, 1986, p. 90.
59. Winograd, N., Kobrin, P. H., Schick, G. A., Singh, J., Baxter, J. P., and Garrison, B. J., *Surf. Sci. Lett.*, **176**, 1817 (1987).
60. Walder, K. T., and Urbassek, H. M., *Appl. Phys. A*, **45**, 207 (1988).
61. Garrison, B. J., *Nuclear Instru. and Methods*, **B**, **17**, 305 (1986).
62. Garrison, B. J., Reimann, C. T., Winograd, N., and Harrison, D. E., *Phys. Rev. B*, **36**, 3516 (1987).
63. Adelman, S. A., *Adv. Chem. Phys.*, **44**, 143 (1980).
64. Tully, J. C., *J. Chem. Phys.*, **73**, 1975 (1980).
65. DePristo, A. E., *Surf. Sci.*, **141**, 40 (1984).
66. Huheey, J. E., *Inorganic Chemistry*, Harper and Row, New York, 1978.
67. Bardoli, R. S., Vickerman, J. C., and Wolstenholme, J., *Surf. Sci.*, **85**, 244 (1979).
68. Winograd, N., Garrison, B. J., and Harrison, D. E., *J. Chem. Phys.*, **73**, 3473 (1980).
69. Holland, S. P., Garrison, B. J., and Winograd, N., *Phys. Rev. Lett.*, **44**, 756 (1980).
70. Winograd, N., Garrison, B. J., and Harrison, D. E., *Phys. Rev. Lett.*, **41**, 1120 (1978).
71. Gibbs, R. A., and Winograd, N., *Rev. Sci. Instru.*, **52**, 1148 (1981).
72. Kobrin, P. H., Schick, G. A., Baxter, J. P., and Winograd, N., *Rev. Sci. Instru.*, **57**, 1354 (1986).
73. Garrison, B. J., Reimann, C. T., Winograd, N., and Harrison, D. E., *Phys. Rev. B*, **36**, 3516 (1987).
74. Castner, D. G., Sexton, B. A., and Somorjai, G. A., *Surf. Sci.*, **71**, 519 (1978).
75. Reimann, C. T., El-Maazawi, M., Walz, K., Winograd, N., Garrison, B. J., and Deaven, D. M., *J. Chem. Phys.*, **90**, 2027 (1989).
76. Demuth, J. E., Christmann, K., and Sanda, P. N., *Chem. Phys. Lett.*, **76**, 201 (1980).
77. Moon, D. W., Winograd, N., and Garrison, B. J., *Chem. Phys. Lett.*, **114**, 237 (1985).
78. Moon, D. W., Bleiler, R. J., Karwacki, E. J., and Winograd, N., *J. Am. Chem. Soc.*, **105**, 2916 (1983).
79. Garrison, B. J., *J. Am. Chem. Soc.*, **104**, 6211 (1982).
80. Foley, K. E., Winograd, N., Garrison, B. J., and Harrison, D. E., *J. Chem. Phys.*, **80**, 5254 (1984).
81. Erley, W., and Wagner, H., *Surf. Sci.*, **74**, 333 (1978).
82. Erley, W., Ibach, H., Lehwald, S., and Wagner, H., *Surf. Sci.*, **83**, 585 (1979).
83. Garrison, B. J., Diebold, A. C., and Lin, J.-H., *Surf. Sci.*, **124**, 461 (1983).
84. Olson, J. A., and Garrison, B. J., *J. Chem. Phys.*, **83**, 1392 (1985); Olson, J. A., and Garrison, B. J., *J. Vac. Sci. Technol.*, **A**, **4**, 1222 (1986).
85. Gibbs, R. A., Holland, S. P., Foley, K. E., Garrison, B. J., and Winograd, N., *Phys. Rev. B*, **24**, 6178 (1981).

86. For a review see Johnston, H. S., *Gas Phase Reaction Rate Theory*, Ronald, New York, 1966, and references therein.
87. Polanyi, J. C., *Acc. Chem. Res.*, **5**, 161 (1972).
88. McCreery, J. H., and Wolken, G., *J. Chem. Phys.*, **60**, 2316 (1977).
89. For a review see Truhlar, D., and Wyatt, R., *Adv. Chem. Phys.*, **36**, 141 (1977).
90. McCreery, J. H., and Wolken, G., *J. Chem. Phys.*, **64**, 2845 (1976).
91. Elkowitz, A. B., McCreery, J. H., and Wolken, G., *Chem. Phys.*, **17**, 423 (1976).
92. Light, J. C., *J. Chem. Phys.*, **40**, 3221 (1964).
93. Pechukas, P., and Light, J. C., *J. Chem. Phys.*, **42**, 3281 (1965).
94. McCreery, J. H., and Wolken, G., *Chem. Phys. Lett.*, **39**, 478 (1976).
95. McCreery, J. H., and Wolken, G., *J. Chem. Phys.*, **65**, 1310 (1976).
96. Gelb, A., and Cardillo, M., *Surf. Sci.*, **59**, 128 (1976).
97. Gelb, A., and Cardillo, M., *Surf. Sci.*, **64**, 197 (1977).
98. Gelb, A., and Cardillo, M., *Surf. Sci.*, **75**, 199 (1977).
99. Lee, C.-Y., and DePristo, A. E., *J. Chem. Phys.*, **84**, 485 (1986).
100. Lee, C.-Y., and DePristo, A. E., *J. Chem. Phys.*, **85**, 4161 (1986).
101. McCreery, J. H., and Wolken, G., *Chem. Phys. Lett.*, **54**, 35 (1978).
102. Diebold, A. C., and Wolken, G., *Surf. Sci.*, **82**, 245 (1979).
103. Tantardini, G. F., and Simonetta, M., *Chem. Phys. Lett.*, **87**, 420 (1982).
104. Kara, A., and DePristo, A. E., *J. Chem. Phys.*, **88**, 2033 (1988).
105. Pfnur, H. E., Rettner, C. T., Lee, J., Madix, R. J., and Auerbach, D. J., *J. Chem. Phys.*, **85**, 7452 (1986).
106. Sexton, B. A., and Madix, R. J., *Chem. Phys. Lett.*, **76**, 294 (1980).
107. Barteau, M. A., and Madix, R. J., *Surf. Sci.*, **97**, 101 (1980).
108. Backx, C., deGroot, C. P. M., and Biloen, P., *Appl. Surf. Sci.*, **6**, 256 (1980).
109. Backx, C., deGroot, C. P. M., and Biloen, P., *Surf. Sci.*, **104**, 300 (1981).
110. Engelhardt, H. A., and Menzel, D., *Surf. Sci.*, **57**, 591 (1976).
111. Bowker, M., Barteau, M. A., and Madix, R. J., *Surf. Sci.*, **92**, 528 (1980).
112. Rovida, G., and Pratesi, F., *Surf. Sci.*, **52**, 542 (1975).
113. Engelhardt, H. A., Bradshaw, A. M., and Menzel, D., *Surf. Sci.*, **40**, 410 (1973).
114. Upton, T. H., Stevens, P., and Madix, R. J., *J. Chem. Phys.*, **88**, 3988 (1988).
115. Martin, R. L., and Hay, P. J., *Surf. Sci.*, **130**, 1283 (1983).
116. Lin, J.-H., and Garrison, B. J., *J. Chem. Phys.*, **80**, 2904 (1984).
117. Tully, J. C., *J. Chem. Phys.*, **73**, 6333 (1980).
118. Girfalco, L. A., and Weizer, V. G., *Phys. Rev.*, **114**, 687 (1959).
119. Binnig, G. K., Rohrer, H., Gerber, Ch., and Stoll, E., *Surf. Sci.*, **144**, 321 (1984).
120. Binnig, G., Rohrer, H., Gerber, Ch., and Weibel, E., *Surf. Sci.*, **131**, L379 (1983).
121. Robinson, I. K., *Phys. Rev. Lett.*, **50**, 1145 (1983).
122. Marks, L. D., *Phys. Rev. Lett.*, **51**, 1000 (1983).
123. Moritz, W., and Wolf, D., *Surf. Sci.*, **163**, L655 (1985).
124. Moller, J., Snowdon, K. J., Heiland, W., and Niehaus, H., *Surf. Sci.*, **178**, 475 (1986).
125. Copel, M., and Gustafsson, T., *Phys. Rev. Lett.*, **57**, 723 (1986).
126. Davenport, J. W., and Weinert, M., *Phys. Rev. Lett.*, **58**, 1382 (1987).
127. Brocksch, H.-J., and Bennemann, K. H., *Surf. Sci.*, **161**, 321 (1985).
128. Foiles, S. M., *Phys. Rev. B*, **32**, 7685 (1985).
129. Foiles, S. M., *Surf. Sci.*, **191**, 329 (1987).
130. Foiles, S. M., and Daw, M. S., *J. Mater. Res.*, **2**, 5 (1987).
131. Foiles, S. M., *Surf. Sci.*, **191**, L779 (1987).
132. Dodson, B. W., *Phys. Rev. Lett.*, **60**, 2288 (1988).
133. Marville, L., and Andreoni, W., *J. Phys. Chem.*, **91**, 2645 (1987).
134. Voter, A. F., and Chen, S. P., *Mat. Res. Soc. Symp. Proc.*, **82**, 175 (1987).

135. Thompson, M. W., *Phil. Mag.*, **18**, 377 (1968).
136. Reimann, C. T., El-Maazawi, M., Walzl, K., Winograd, N., Garrison, B. J., and Deaven, D. M., *J. Chem. Phys.*, **89**, 2539 (1988).
137. Lo, D. Y., Tombrello, T. A., Shapiro, M. H., Garrison, B. J., Winograd, N., and Harrison, D. E., *J. Vac. Sci. Technol. A*, **6**, 708 (1988).
138. Schlier, R. E., and Farnsworth, H. E., *J. Chem. Phys.*, **30**, 917 (1959).
139. Redondo, A., and Goddard, W. A., *J. Vac. Sci. Technol.*, **21**, 344 (1982).
140. Chadi, D. J., *Phys. Rev. Lett.*, **43**, 43 (1979).
141. Yin, M. T., and Cohen, M. L., *Phys. Rev. B*, **24**, 2303 (1981).
142. Yang, W. S., Jona, F., and Marcus, P. M., *Phys. Rev. B*, **28**, 2049 (1983).
143. Tromp, R. M., Hamers, R. J., and Demuth, J. E., *Phys. Rev. Lett.*, **55**, 1303 (1985).
144. Hamers, R. J., Tromp, R. M., and Demuth, J. E., *Phys. Rev. B*, **34**, 5343 (1986).
145. Pollman, J., Kalla, R., Kruger, P., Mazur, A., and Wolfgang, G., *Appl. Phys. A*, **41**, 21 (1986).
146. Eastman, D. E., *J. Vac. Sci. Technol.*, **17**, 492 (1980).
147. Rowe, J. E., and Phillips, J. C., *Phys. Rev. Lett.*, **32**, 1315 (1974).
148. Mark, P., Levine, J. D., and McFarlane, S. H., *Phys. Rev. Lett.*, **38**, 1408 (1977).
149. Levine, J. D., McFarlane, S. H., and Mark, P., *Phys. Rev. B*, **16**, 5415 (1977).
150. Pandey, K. C., *Phys. Rev. Lett.*, **47**, 1913 (1981).
151. Chadi, D. J., *Phys. Rev. B*, **26**, 4762 (1982).
152. Pandey, K. C., *Phys. Rev. Lett.*, **49**, 223 (1982).
153. Joyce, B. A., *Rep. Prog. Phys.*, **37**, 363 (1974).
154. Cho, A. Y., and Arthur, J. R., *Prog. Sol. State Chem.*, **10**, 157 (1975).
155. Panish, M. B., *Science*, **208**, 915 (1980).
156. Dohler, G. H., *Sci. Am.*, **249**, 144 (1983).
157. Joyce, B. A., Bradley, R. R., and Booker, G. R., *Philos. Mag.*, **15**, 1167 (1967).
158. Abbink, H. C., Broudt, R. M., and McCarthy, G. P., *J. Appl. Phys.*, **39**, 4673 (1968).
159. NoorBatcha, I., Raff, L. M., and Thompson, D. L., *J. Chem. Phys.*, **81**, 3715 (1984).
160. NoorBatcha, I., Raff, L. M., and Thompson, D. L., *J. Chem. Phys.*, **82**, 1543 (1985).
161. NoorBatcha, I., Raff, L. M., and Thompson, D. L., *J. Chem. Phys.*, **83**, 6009 (1985).
162. Kasper, E., *Appl. Phys. A*, **28**, 129 (1982).
163. Aizaki, N., and Tatsumi, T., *Surf. Sci.*, **174**, 658 (1986).
164. Khor, K. E., and Das Sarma, S., *Chem. Phys. Lett.*, **134**, 43 (1987).
165. Gawlinski, E. T., and Gunton, J. D., *Phys. Rev. B*, **36**, 4774 (1987).
166. Brenner, D. W., and Garrison, B. J., *Surf. Sci.*, **198**, 151 (1988).
167. Schneider, M., Rahman, A., and Schuller, I. K., *Phys. Rev. Lett.*, **55**, 604 (1985).
168. Gossman, H.-J., and Feldman, L. C., *Phys. Rev. B*, **32**, 6 (1985).
169. See for example, Feldman, L. C., Mayer, J. W., and Picraux, S. T., *Materials Analysis by Ion Channeling*, Academic, New York, 1982.
170. Zuhr, R. A., Alton, G. D., Appleton, B. R., Herbots, N., Noggle, T. S., and Pennycock, S. J., in *Materials Modification and Growth Using Ion Beams* (Eds U. J. Gibson, A. E. White and P. P. Pronko), Materials Research Society, Pittsburgh, 1987, p. 243.
171. Dodson, B. W., *Phys. Rev. B*, **36**, 1068 (1987).
172. Garrison, B. J., Miller, M. T., and Brenner, D. W., *Chem. Phys. Lett.*, **146**, 553 (1988).
173. Raff, L. M., NoorBatcha, I., and Thompson, D. L., *J. Chem. Phys.*, **85**, 3081 (1986).
174. Rice, B. M., NoorBatcha, I., Thompson, D. I., and Raff, L. M., *J. Chem. Phys.*, **86**, 1608 (1987).
175. Froitzheim, H., Lammering, H., and Gunter, H. L., *Phys. Rev.*, **B 27**, 2278 (1978).
176. Brenner, D. W., *J. Mat. Res. Soc. Symp. Proc.*, 1988, in press.

177. Brenner, D. W., unpublished.
178. Brenner, D. W., Elert, M. L., Walker, F. E., and White, C. T., unpublished.
179. Kirkpatrick, S., Gelatt, C. D., and Vecchi, M. P., *Science*, **220**, 671 (1983).
180. Car, R., and Parrinello, M., *Phys. Rev. Lett.*, **55**, 2471 (1985).
181. Car, R., and Parrinello, M., *Phys. Rev. Lett.*, **60**, 204 (1988).
182. Ballone, P., Andreoni, W., Car, R., and Parrinello, M., *Phys. Rev. Lett.*, **60**, 271 (1988).
183. Payne, M. C., Joannopoulos, J. D., Allan, D. C., Teter, M. P., and Vanderbilt, D. H., *Phys. Rev. Lett.*, **56**, 2656 (1986).
184. Payne, M. C., Bristowe, P. D., and Joannopoulos, J. D., *Phys. Rev. Lett.*, **58**, 1348 (1987).
185. Needels, M., Payne, M. C., and Joannopoulos, J. D., *Phys. Rev. Lett.*, **58**, 1765 (1987).
186. Allan, D. C., and Teter, M. P., *Phys. Rev. Lett.*, **59**, 1136 (1987).
187. Pederson, M. R., Klein, B. M., and Broughton, J. Q., *Phys. Rev. B*, **38**, 3825 (1988).
188. Sprik, M., and Klein, M. L., *J. Chem. Phys.*, **87**, 5987 (1987).
189. Sprik, M., and Klein, M. L., *J. Chem. Phys.*, **89**, 1592 (1988).
190. Allen, R. E., and Menon, M., *Phys. Rev. B*, **33**, 5611 (1986).
191. Menon, M., and Allen, R. E., *Phys. Rev. B*, **33**, 7099 (1986).
192. Sankey, O. F., and Allen, R. E., *Phys. Rev. B*, **33**, 7164 (1986).
193. Riley, M. E., Coltrin, M. E., and Diestler, D. J., *J. Chem. Phys.*, **88**, 5934 (1988).
194. Berendsen, H. J. C., Postma, J. P. M., van Gunsteren, W. F., DiNola, A., and Haak, J. R., *J. Chem. Phys.*, **81**, 3684 (1984).
195. Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H., and Teller, E., *J. Chem. Phys.*, **21**, 1087 (1953).
196. Voter, A. F., and Doll, J. D., *J. Chem. Phys.*, **80**, 5832 (1984).
197. Voter, A. F., and Doll, J. D., *J. Chem. Phys.*, **82**, 80 (1985).
198. Voter, A. F., *J. Chem. Phys.*, **82**, 1890 (1985).