Modeling the full monty: baring the nature of surfaces across time and space

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Abstract

Computational materials research has made great strides in recent years in the description of the science of surfaces and interfaces. So far, however, the approaches generally have been limited to fixed resolutions of time and space. In effect, each group of scientists has chosen its specific scale for the "road maps" used by them to investigate surfaces and interfaces, some focusing only on highly resolved "city maps", others considering the big picture of the "countrywide" view. So, just as in the planning for improvements of, e.g., a nation's infrastructure, future progress in the field requires limitations of the models to single length and time scales to be overcome. Recently, the first steps have been taken to set up multi-scale modeling techniques, often involving collaborations of chemists, physicists, and engineers. Here, it is our aim to present a representative survey of these techniques. In particular, we discuss informed continuum approaches, the quasicontinuum method, the kinetic Monte Carlo technique and accelerated molecular dynamics simulation. We show where they have been used to date and outline where their future application holds promise. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Picture a microscope where, with a twist of a knob, one sees first a smooth solid surface, then, zooming in, one notices cracks in the solid, or perhaps dust particles, or, in a liquid droplet, some cells. Zooming in further, suppose our microscope sees what is on the surface or in the crack or in the cells, in the form of islands or steps or molecules, comprised of atoms, which are, in turn, composed of electrons and nuclei. We have just described a multi-scale picture of an object of interest, where the "scale" here is size or "length".

Over the course of the last century, improvements in instrumentation have made it possible to observe all these scales. The smaller length scales, right down to the atom on a surface, have become accessible only recently, for example, through the invention of the scanning tunneling microscope [1,2]. For the interpretation of most of the observations, companion calculations are necessary. It

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has been common practice to deduce theories separately for each of the length scales observed. On the smallest scales, where electrons and nuclei are visible, the effects of quantum mechanics have been taken into account; on larger scales classical and statistical mechanics (with the quantum effects hidden in empirical parameters) was generally sufficient to explain the experiment. Progress in computational materials science in the last two decades made possible ever more precise predictions of properties on these separate length scales. With the beginning of the new millenium, the borders between theories (and theorists) describing different scales are beginning to dissolve, and a more unified look at materials science is beginning to emerge. Chemists, physicists and engineers working in the field of theoretical materials science find it advantageous (or even necessary) to collaborate, and find that connections can and should be made across scales, from big to small, so we can know how small affects big, and vice versa. This new "multi-scale" approach sharpens the theoretical understanding of the interconnectedness of processes observed by our "microscope" on the different length scales and is referred to as multi-scale modeling. Wherever necessary, observables such as energies are calculated by treating individual atoms with quantum mechanics. Wherever possible, large numbers of atoms are treated with coarser techniques, e.g., by taking average values to determine their behavior as a subunit of the whole system. In between these descriptions, there can be 10 orders of magnitude from the atomic length scale (10^{-10} m) to the chunk of steel length scale (1 m). To describe certain properties of some materials, it may be necessary to consider at the same time the tiny realms of quantum physics and quantum chemistry and the macroscopic partitions of materials considered in, for example, finite element methods of mechanical engineering [3].

In the same way, in the time domain, single ultra-short events, such as vibrational motion or the breaking of a bond at a surface, should be treated at least partially by quantum mechanics. For example, the evolution of a moderately sized system (typically tens of atoms) can be described using the "ab initio" molecular dynamics approach (integrating Newton's classical equations of motion using the forces calculated including quantum mechanical effects) for extremely short time periods, currently extending to picoseconds at most [4]. So while this approach can describe how ultra-short events unfold, it is insufficient to describe processes happening on time scales of seconds or more, such as the growth of a material by the adsorption (sticking to the surface) of atoms and molecules from the gas phase. To satisfy these aims, it is necessary to use coarser methods that, in their more advanced realizations, make use of the quantum mechanical results for the description of single events, that comprise the overall phenomenon.

Many chemical processes happen at surfaces and interfaces, where different materials in different phases (solid, liquid, gaseous) come together. When the different length scales are taken into account, more realistic and complete descriptions can be achieved for a wide range of behavior. These include surface phase transitions and reconstructions (structural reorganizations), surface and interface strain, dislocation (a long-range defect, such as a missing row of atoms) formation, materials growth and etching, and chemically induced materials failure, e.g., embrittlement or corrosion, in which a material is attacked at a surface and weakened so that it may crack under stress. In the time domain, rates can vary by ten powers of ten or more, e.g., in materials growth and surface melting, in adsorption and desorption (release from the surface), in biological processes, and in catalytic reactions or cooperative phenomena such as oscillating reactions.

It is our intention to give a description of the general concepts of current multi-scale modeling techniques and then to focus on their application to the investigation of surfaces and interfaces. We give examples and describe results that have been and can only be obtained by multi-scale modeling. We do not attempt to provide details on every method. The techniques discussed are intended to illustrate the basic ideas behind multi-scale modeling: informed continuum methods, where macroscopic material constants are determined from lower length scales (including from quantum mechanics); the quasicontinuum method, which links atomistic and continuum approaches on-the-fly;

the kinetic Monte Carlo technique, which allows one to reach arbitrarily long time scales (at the expense of full determinism); and accelerated molecular dynamics techniques, which simulate the evolution of many-particle systems by making rare events happen at a faster pace. We close with some suggestions for future research.

2. Theory of the multi-scale modeling of surfaces

Obviously, all real-life objects have surfaces. However, for the determination of many material properties, it is often assumed that the material is infinite in all directions. (Additionally it is often assumed that it is comprised of perfectly periodic units (see the unit cell of a body-centered cubic (bcc) crystal shown in Fig. 1), which neglects all the real-life defects in solids such as missing atoms, impurities, incorrectly placed atoms, cracks, dislocations, grain boundaries, etc.) In many objects, the assumption of infinite expanse makes sense when observed on the atomic level: In a macroscopic chunk of material, almost all the atoms are far away from the surface. The distance from the surface is so large that it no longer influences the local region around the inner atoms: For all practical purposes they "see" an infinite solid.

Indeed, a cube of 1 cm edge length contains about 10^{23} atoms, while there are only $\sim 10^{16}$ atoms on its surface. Although the latter certainly is a large number, a factor of 10 million separates the two numbers—and the volume-to-surface ratio becomes larger as the size of the body increases. Thus, in many applications the surface can be neglected.

Things are different, however, in other instances. On modern computer chips, so much functionality has been crowded onto so tiny a space that wires are only a few hundred or thousand atoms in diameter—and miniaturization is expected to continue. In fact, in nanometer-size (1 nm = 10^{-9} m; e.g., the diameter of a hydrogen atom is 0.1 nm) structures, e.g., nanoporous materials such as zeolites, which often are used as "molecular sieves", the number of surface atoms can be comparable to or even exceed the number of bulk atoms. Surface effects dominate the behavior of these materials, so their correct description becomes crucial. Surface effects also are important when it comes to interactions of materials with the outside world. These interactions usually take place at or near surfaces and can occur through electromagnetic radiation (light) or single atoms, molecules, liquids or other solids. The area of materials growth and etching, important, for example, in the design of nanoscale wires and microscale motors, requires consideration
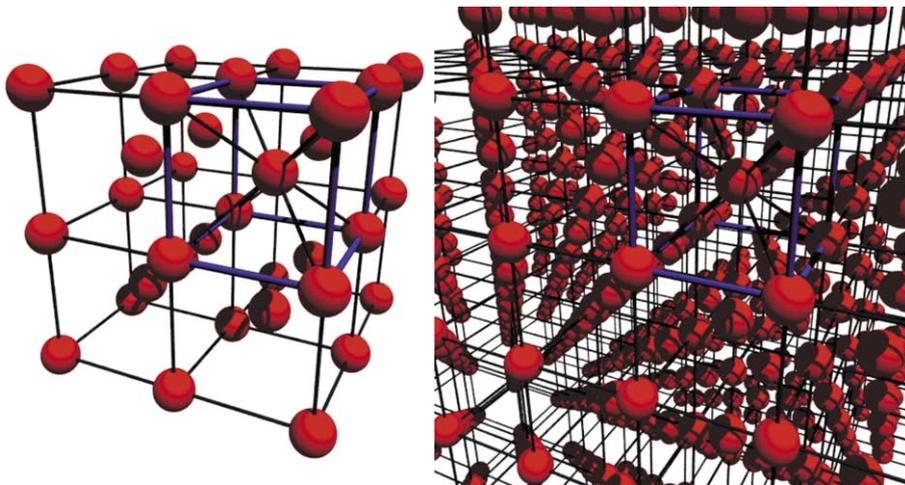

Fig. 1. Left: The unit cell of a body-centered cubic (bcc) lattice (blue) and seven other unit cells (grey). The atoms are denoted by red spheres. Right: A larger representation of a bcc crystal. Elements that crystallize in this structure include chromium (Cr), iron (Fe) and sodium (Na).
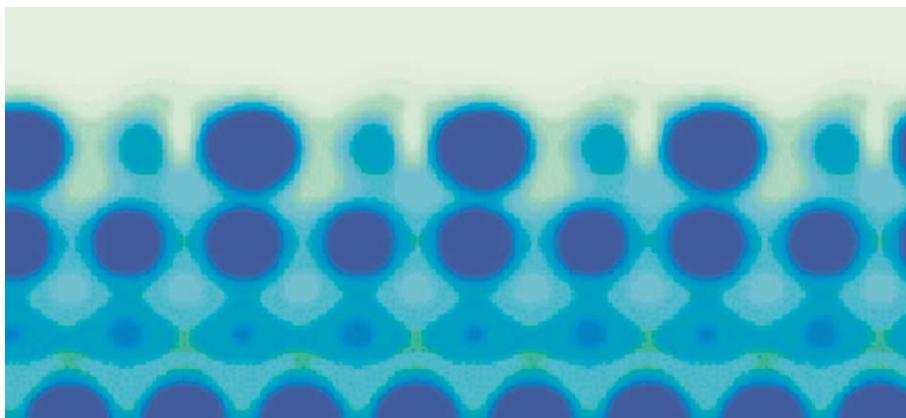
Fig. 2. The electron charge density at a surface and an interface: a monolayer film of Al_2O_3 on Ni. The darker the color, the higher is the probability of finding an electron at that position. The white area on the top indicates vacuum; the top layer is alumina (Al_2O_3) with the O atoms (big blue regions) close to the cross-section, the Al atoms further away (smaller, lighter blue regions). The lower three layers are composed of nickel (Ni) atoms, the middle layer being out of the paper plane. (Figure courtesy of E.A. Jarvis, from a density functional theory calculation [91].)

of the surface by definition. In catalytic reactions, the catalyst is a material that accelerates the rate of a chemical reaction without being consumed or essentially altered. In the case of heterogeneous catalysis, the reaction takes place at the surface and the bulk is irrelevant.

Computational science has developed a number of methods to determine theoretically the properties of solids and their surfaces. We next give a general introduction to these methods, describe the approaches used to model surfaces, and present the theory behind relevant multi-scale modeling techniques.

2.1. Computational materials science

Computational materials science aims to predict the properties of materials via computer simulation. Computers are used to solve the equations that govern the way the building blocks of matter interact. At the highest resolution considered, these building blocks are atoms composed of nuclei and electrons. The nuclei are generally well approximated as positive point charges, while the electrons are described by a negative charge distribution spread out in space. The extremely small mass of the electrons makes it necessary to describe them using quantum mechanics. In the quantum world,

speed and position of low mass particles cannot be known exactly at the same time, as expressed in Heisenberg's uncertainty principle. One can determine, however, the probability for the electrons to be at a specific point in space. This quantity is called the charge density, and it can be measured experimentally by X-ray diffraction. Fig. 2 shows the charge density for a cross-section of a metal–ceramic interface and a crystal surface. The dark areas indicate a high electron density (the charge density of the electrons), which can be found near the nuclei and in certain strong bonds between atoms. Materials are typically electrically uncharged, hence the sums of the positive nuclear and the negative electronic charges cancel. In a typical solid, there are $\sim 10^{23}$ atoms/cm^3 and each atom contributes a number of electrons to this many-particle system. The large number of particles generally means that approaches to solving the many-particle problem at the fundamental level do not yield correct quantitative results. Yet, the vast calculation power of modern computers can be used to determine approximate numerical solutions. It should be noted, though, that even with the most powerful computers and the most advanced techniques, an explicit, exact description of the many-particle electron system is not possible. Clever approximations have been invented

to deal with this problem. We next outline an important subset of the methods developed to describe properties of solids, surfaces and interfaces, and their interaction with the environment: electronic density functional theory and quantum chemistry for describing electrons and nuclei, molecular dynamics and Monte Carlo "atomistic" methods, and continuum theory of macroscopic solids.

Within computational materials science, three disciplines intersect: those of computational solid state physics, theoretical chemistry, and mechanical engineering. Each field is wide by itself and the boundaries are sometimes fuzzy. The following definitions give an idea of the primary contributions of each of the disciplines to materials science. Theoretical solid state physics is concerned with rendering as accurately as possible the geometric and the electronic structure of a given solid. The geometric structure is given by the positions of the atoms, the electronic structure by the energies electrons have in the solid and their wave function. (The wave function completely describes the electrons' behavior. Among other properties, it provides the charge density.) In theoretical surface chemistry, the main aim is to model atomic and molecular adsorption, desorption, diffusion (movement along and in the surface) and reactions occurring at solid surfaces. Important aspects are identifying the ways a certain reaction can happen (its mechanism) and the relative likelihood for each of these pathways to be traversed (reaction rates). In treating atoms or molecules interacting with crystals, it becomes necessary to treat non-periodic entities within or near periodic ones, each of which are described differently. While physicists often tend to use methods that are developed to treat periodic solids, chemists tend to employ techniques that are optimized to describe molecules. Mechanical engineers, on the other hand, usually deal with questions of stability and durability of materials. Traditionally, they have ignored the atomic structure of solids. Rather, they consider average mechanical properties to determine how large structures of material, from bridges to airplane wings, may behave under stress. Recently, however, the calculations have begun to include atomic scale modeling. One ex-

ample of this is the quasicontinuum method, discussed later.

Theoretical predictions are most convincing when they are calculated with as few empirically determined parameters as possible. In materials theory, the only parameter that must be supplied is the makeup of the solid to be studied, i.e., which elements comprise the material and, preferably, in which approximate geometry they are arranged. A method that takes only these external data as input and computes the geometric and electronic structure based on the laws of quantum mechanics is called an ab initio, or first-principles, method. These methods are usually costly computationally and currently are restricted to the treatment of crystals made up of unit cells of at most a few thousand (and more typically, $\sim$10–100) atoms, corresponding to a cube of $\sim 10^{-20}$ cm^3 volume. Unit cells are groups of atoms that are treated as the building blocks of the crystal; the unit cells are repeated identically through space to create the atomic structure of the crystalline solid (see Fig. 1). Significantly less burdensome computationally are so-called empirical or semi-empirical methods. Empirical methods employ parameters based on experimental values; semi-empirical techniques are based on results from both experiment and ab initio approaches.

One successful ab initio method for the determination of the electronic and the geometric structure of materials is density functional theory [5]. Within density functional theory, the problem of finding a description for all the electrons in the solid is reduced to the problem of determining the correct electron density. Hohenberg and Kohn showed that all the ground state properties of a system of electrons can be determined from its charge density alone (where "ground state" refers to the lowest energy state the system can be in). This is an enormous simplification, since the electron density is a function of merely three position variables, such as x, y and z, whereas the wave function describing the electrons themselves depends on the coordinates of all the electrons. The total energy of all the electrons is the sum of the kinetic energy (the energy of motion) of all the electrons, the Coulomb energy due to their attraction to the positive nuclei, the Coulomb energy

due to the repulsion of the negative electrons amongst themselves, and the non-classical, exchange-correlation energy (a term that lowers the energy due to the electrons' tendency to avoid each other). The local density approximation for the last contribution yields a convenient set of single-electron equations to determine the electron density [6]. In a number of cases, an approximation to the exchange-correlation energy that not only depends on the electron density (as in the local density approximation) but also on its gradient has been found to improve results (generalized gradient approximation [7]). In the single-electron approximation, the wave function is determined for a single electron moving subject to a potential due to the nuclei and the other electrons. Density functional theory has certain limitations, particularly when it comes to calculating not the ground state but states with higher energies, or excited states. However, the list of successful applications of density functional theory within the local density approximation (and generalized gradient approximation) to condensed matter phenomena is long and impressive. Unfortunately, conventional density functional theory algorithms become very slow and cumbersome when the unit cells become large. The computational time required for the calculation of the electron energies scales with the number of electrons, n, to the third power. While one might expect that a system twice as large should only cost twice as much to calculate, a density functional theory calculation would be eight times as costly (2^3). Physically, one might expect the cost of models to scale linearly with size of the system. Algorithms which achieve a linear dependence on n are dubbed "linear scaling," or $O(n)$ (pronounced "order n"), methods [8,9].

In quantum chemistry, the system of electrons within each atom or molecule is described by a many-electron wave function. There are several stages of approximation and different approaches for the way these wave functions are constructed from single-electron solutions ("orbitals"). The typical starting point is Hartree–Fock theory [10], where the wave function, a product of orbitals, is constructed to obey certain fundamental laws of quantum mechanics, namely the Pauli exclusion principle, which prohibits electrons (of the same

spin) from occupying the same region of space. In any system, such as an atom with a nucleus and electrons, nature demands a minimum total energy, which involves a compromise between kinetic energy and potential energy. (The potential energy describes the energy stored in a system, usually depending on the relative position of, e.g., electrons or atoms. The term "potential" is used for the potential energy given as a function of spatial coordinates.) The electron–electron Coulomb repulsion energy is always positive, and therefore nature acts to minimize it, so long as the kinetic energy does not rise too steeply as a result. Nature reduces electron–electron repulsion by correlating the motion of the electrons so as to keep them as far apart from each other as possible at all times. Thus, the many-particle wave function should contain electron correlation. This is done in the so-called configuration interaction approach. Other techniques that model the correlation of electronic motion and the reduction of the Coulomb repulsion include many-body perturbation theory and the coupled cluster method (see, e.g. Ref. [10]). Modern quantum chemistry methods can yield accurate results, but the scaling of the computation with the number of electrons prohibits their use for more than tens of atoms. Recent advances have reduced the scaling of some of these methods to near linear, but their overall cost is still high [11,12].

The molecular dynamics technique allows one to follow the evolution of a collection of atoms through time. Based on the velocities of the atoms and the forces between them, the trajectories (time-evolving positions) of all the atoms are calculated. Systems of interest for surface chemistry are atoms and molecules near surfaces in such processes as scattering, catalytic reactions, growth, and etching. Fig. 3 shows the elementary processes which happen when molecules interact with surfaces: adsorption, dissociation, diffusion, reaction, and desorption. In surface simulations, the atoms inside the solid, far away from the surface, are close to their equilibrium positions (i.e., the positions the atoms adopt after they have moved according to the forces acting on them and the forces have balanced out). However, dramatic reconfigurations of the surface atoms may happen. In molecular dynamics, the electrons are usually not
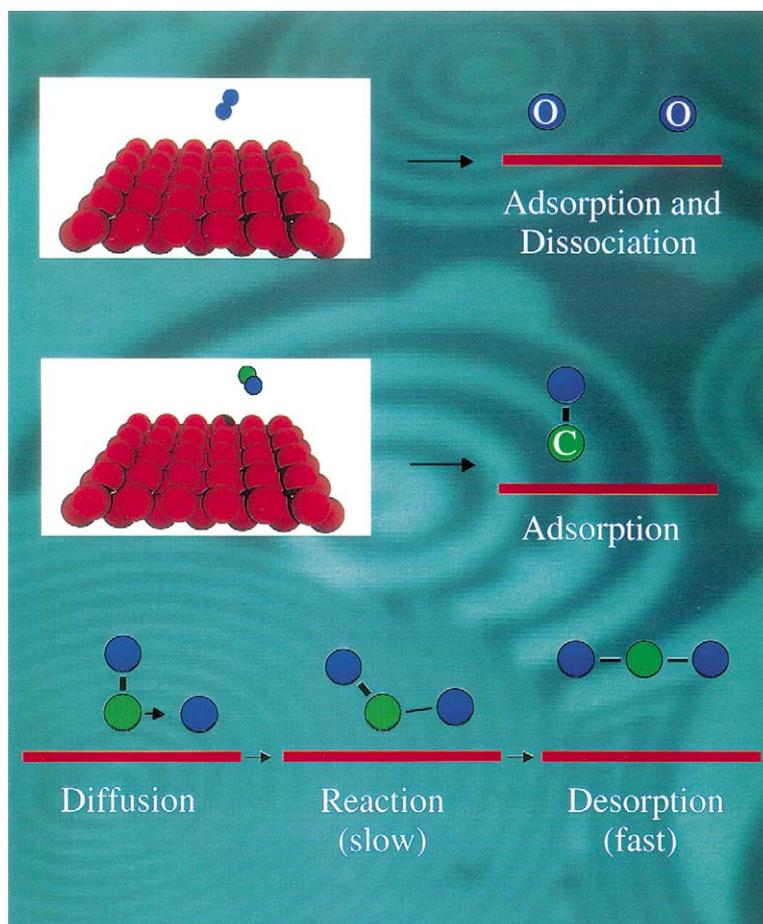
Fig. 3. The fundamental steps of the catalytic oxidation of carbon monoxide (CO) on a platinum surface. The two upper panels show oxygen being molecularly adsorbed and dissociating easily on the surface. Middle panels: CO is molecularly adsorbed. In the lower three panels, CO diffuses on the surface and meets an oxygen atom (left), CO reacts slowly with the oxygen atoms (middle), but the resulting carbon dioxide desorbs quickly from the surface (right). This reaction generates complex patterns of the oxygen and CO concentrations on the platinum surface. In the spatial pattern displayed in the background (whose width corresponds to about 0.2 mm) the dark areas are covered by oxygen, the light areas by CO (courtesy of G. Ertl [93]).

explicitly considered for the interaction among atoms. Molecular dynamics techniques still take the individual atoms into account, but typically via an empirical analytic interaction potential, which allows forces to be evaluated cheaply. In this way up to millions of atoms can be followed, especially when parallel processing is used to split up the solid into subsystems [13]. By contrast, the more accurate ab initio molecular dynamics accounts for the relaxation of the electrons as the atoms move, and thus is significantly slower [4,14,15].

An example of the predictive power of the molecular dynamics technique for surface chemistry is given by ab initio-derived molecular dynamics calculations (a modest multi-scale model, where parameters describing the atomic interactions ($\sim10^{-9}$ m) were obtained not from experiment but from quantum mechanical ($\sim10^{-10}$ m) calculations) of the chemisorption of fluorine atoms and molecules on a silicon surface. A number of predictions made about the chemisorption processes [16–18], some of them in direct contravention of

contemporary chemical thinking, were confirmed in later experiments [19–23]. In particular, these simulations characterized quantitatively two reaction pathways (atom abstraction by the surface and dissociative adsorption) as a function of how fast the molecules hit the surface and of how the molecules are oriented as they impinge on the surface [17]. Defying conventional wisdom, the less exothermic (heat-releasing) pathway of atom abstraction dominates for slow molecules, while dissociative adsorption is preferred only by fast molecules (experimental confirmation reported in Refs. [20,22]). The molecular dynamics simulations [17] predicted that abstraction and dissociation go through a common intermediate, whereby dissociation occurs stepwise through abstraction followed by release of a halogen atom that either goes into the gas phase or quickly finds a nearby Si atom on which to bind (confirmed experimentally in Ref. [21]). Conventional dissociative adsorption is thought to happen with both atoms of a diatomic molecule simultaneously attaching to a surface, but in this case the "dangling bonds" (localized single electrons) of Si alter the reaction mechanism. These molecular dynamics simulations [18] further showed that when halogen atoms are released into the gas phase, they come off at an angle with respect to the surface normal and rather slowly, losing considerable energy to the solid (measured in Ref. [23]). Finally, molecular dynamics simulations of high-pressure etching [16] showed that local heating of the surface, due to strong chemical bond formation, disorders the Si crystal, which was subsequently confirmed by experiment [19]. On a practical note, the theory culminated [18] in a suggestion for a two-cycle etching process; a related process is now used commercially [24].

Monte Carlo methods are frequently used to simulate physical events based on their *probabilities* (related to either thermal equilibrium or kinetic rates). The name is derived from the famous casino in the Mediterranean seaport of Monaco and points to the use of random numbers, as in the outcome of spinning a roulette wheel. One use of Monte Carlo methods is the study of equilibrium properties of matter (a system in equilibrium remains in that state unless acted upon by some

external influence), e.g., the equilibrium structures of surfaces and interfaces [25–27]. At a given temperature, atoms within a condensed phase move in an unorganized manner. If the solid or liquid is not in an equilibrium structure, it evolves towards one. The rearrangements of the atoms, and thus the evolution of the system, can be simulated by Monte Carlo. For the move toward equilibrium, the system evolves not only simply to lower energy states (which, of course, occurs) but changes states according to so-called Boltzmann probabilities [28] that allow access to higher energy states. These probabilities depend strongly (exponentially) on the ratio of the energy difference between states to the thermal energy, the latter of which is proportional to the temperature. Boltzmann probabilities have the characteristic that the probability of changing state increases with temperature and, that the more energy required, the less likely it is that the system can provide this energy for the process to happen. If the system is in a lower energy state after a process occurs, it is less likely to leave it than the former state, because more energy would be required to escape. However, the Boltzmann probabilities allow the system to eventually rearrange itself into another state, that may be even more favorable energetically. After a sufficiently long simulation time, the system reaches equilibrium, where a stable structure is achieved.

An example for the description of *non*-equilibrium systems by Monte Carlo is the growth of films on surfaces [29]. Because actual film growth occurs much more slowly (one layer per second) than one can simulate with, e.g., molecular dynamics (typical time scales of nanoseconds instead of seconds), one means to model film growth is by "equilibrating" the system between each adsorption of an atom, using Monte Carlo. In particular, atoms can be deposited randomly on the surface, changing the state of the system. The evolution is again modeled by Monte Carlo using Boltzmann probabilities for the rearrangement of atoms on or near the surface. If the equilibration "time" between depositions of atoms is sufficiently large, the current system, real or simulated, may reach an equilibrium state which is destroyed by the next deposition. The process is repeated until the desired film thickness is reached.

In engineering, a common approximation is to ignore the discrete nature of solids and to assume a continuity of structure. Every volume of the continuum solid, at all length scales, is assumed to exhibit the properties observed in the macroscopic material. For example, if a certain coefficient of elasticity is measured for a rod of steel of 1 m length, this coefficient is assumed be valid for all portions of the rod, be they 1 cm long or 1 $\mu m = 10^{-6}$ m. (Linear elasticity means in the case of a spring that the counteracting force is proportional to the extension away from equilibrium.) At the atomic and molecular length scale, however, this assumption no longer holds. For many applications, though, the equations of continuum mechanics can be used safely to describe deformations of solids. In continuum mechanics, few material parameters (e.g., elastic constants) are needed to describe how the solid reacts to applied stress or pressure.

In mechanical engineering and other fields, material behavior is frequently simulated by finite element methods, which are numerical techniques for obtaining the response of physical systems to external influences. In these methods, a solid is divided into little space-filling polyhedra of finite volume whose corners are called nodes. In the two-dimensional example shown in Fig. 4(b), these polyhedra are triangles which cover the square piece of material. A cut is used to simulate a crack whose evolution is studied by simulating forces on the material. The finite elements are thought of as continuum particles [30], representing a large number of atoms (e.g., $\sim 10^6$). During the finite element simulation, the value of an unknown function (such as the displacement of each of the nodes covering the piece of material when considering the response of, e.g., a steel beam to forces, or a temperature distribution in a simulation of, e.g., an engine part in a gas turbine) is determined at each node by minimizing the energy over the whole body, taking into account material parameters and the sharing of the boundaries of the finite elements. At the same time, the number of nodes can be adjusted to account for spatially varying forces that may act on the body, possibly leading to its deformation. Sophisticated algorithms have been invented to refine adaptively the
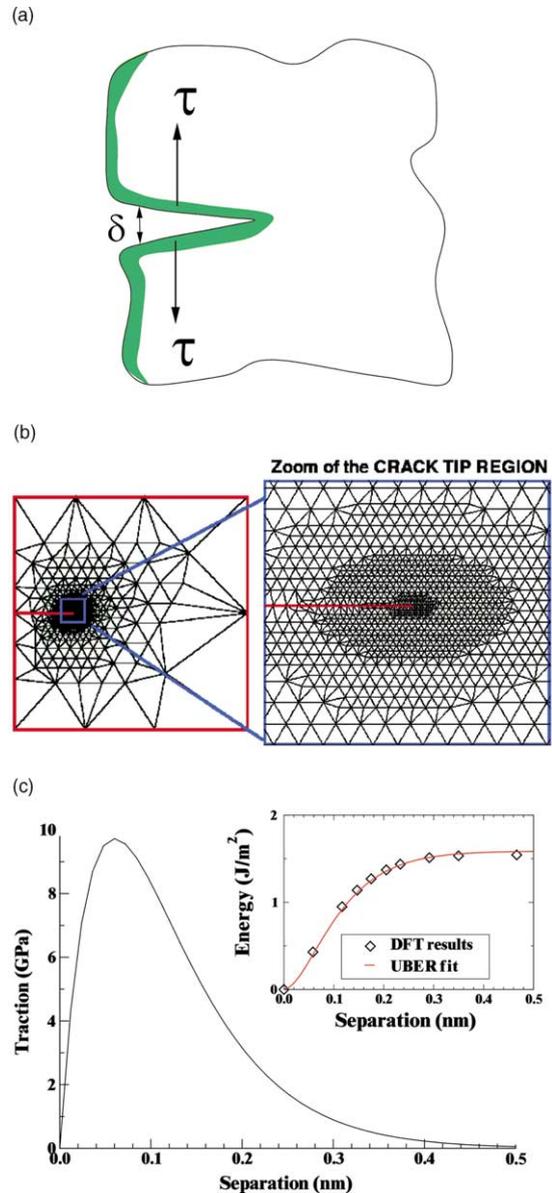

Fig. 4. Panel (a): A schematic of the forming of a crack. Applied is a traction τ (applied force per unit area) and the separation δ is the distance between the surfaces. Bulk aluminum (Al, white) oxidizes to alumina (Al_2O_3, green) at the surface. Panel (b): A finite element/cohesive zone model in which results derived from density functional theory are used to describe crack formation (courtesy of M. Ortiz). Panel (c): The calculated traction is shown as a function of the separation, as derived from a universal binding energy relation (UBER) [94] fitted to density functional theory-generalized gradient approximation results for unrelaxed surfaces (inset) [71] (courtesy of R.L. Hayes).

element mesh in regions where the solution is expected to vary strongly, while a coarser mesh is kept in regions where the solution is varying slowly [31].

2.2. Surface modeling

At the atomic scale, objects with surfaces are more difficult to describe than objects with full three-dimensional periodicity. A number of approaches have been developed to treat surfaces on the atomic level (see Fig. 5). In the description closest to the actual surface geometry, the system is treated as a semi-infinite crystal where the periodicity holds inside the solid (shown schematically in Fig. 5(b)). Several methods have been developed

to calculate the electronic properties of the semi-infinite crystal (e.g., Refs. [32–34]).

In other approaches, the surface is treated as a so-called slab. In the "stand-alone" geometry (Fig. 5(c)) this is a single film of several layers of atoms with vacuum on both sides (see, e.g., Ref. [35]). The slab geometry necessarily leads to the existence of two surfaces, both of which can be taken into account, or the "bottom" layer of the slab can be fixed to the bulk structure.

A large number of electronic structure methods have been designed with three-dimensional periodicity in mind. This allows the use of so-called fast Fourier transform routines [36] to evaluate certain properties (such as the classical electron–electron Coulomb repulsion). Three-dimensional
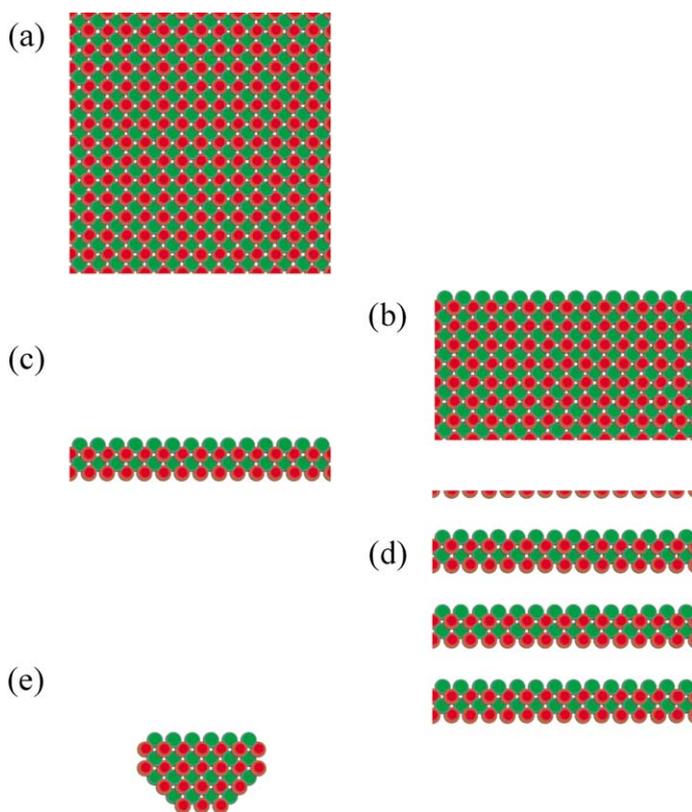

Fig. 5. Several geometries used to simulate surfaces of crystals, shown here for the zincblende crystal, suppressing the dimension perpendicular to the page: Panel (a): bulk, panel (b): half-space, panel (c): single slab, panel (d): super-cell slab, and panel (e): cluster geometries. (The geometries shown are only schematic; generally, in panels (c) and (d) the slabs have to be thicker, as do the vacuum regions in panel (d); also the cluster in panel (e) consists generally of a smaller number of atoms.)

periodicity also makes possible the use of plane-waves ($\exp[i\mathbf{k} \cdot \mathbf{r}]$) rather than more complicated functions, to construct the wave function. Due to the periodicity of the crystal, the wave functions fulfill a mathematical condition, called Bloch's theorem, which plane waves account for by default. To mimic a surface while retaining periodicity in the third dimension, the "super-cell" slab approach can be used: Here, an infinite number of parallel slabs separated by vacuum layers is simulated (Fig. 5(d)). The computational cost is reduced by using thin slabs and thin vacuum layers. The slab has to be thick enough to simulate the bulk crystal beneath the surface, and both the slab and the vacuum layer have to be sufficiently thick to prevent the surfaces from interacting with each other across either layer—they must not "know" of the existence of the other surfaces. In practice, the unit cells employed are chosen to be as small as possible in the directions parallel to the surface as well. The size of the cell in this lateral dimension is dictated by, e.g., the coverage of adsorbates on the surface.

An alternative approach in common use with quantum chemistry techniques, is to use a cluster to model the surface (Fig. 5(e)). In the cluster model, only a small number of surface and sub-surface atoms are treated, while the rest of the solid is neglected. For this smaller number of atoms, accurate results may be obtained using, e.g., configuration interaction techniques of quantum chemistry (see, e.g., Ref. [37]). The challenge is to minimize the influence of the artificial surfaces created by the finite size of the cluster [38].

A compromise between super-cell slab and finite cluster models is to use an embedding model. In embedding methods, a cluster of atoms is treated separately from a larger number of background atoms in which they are "embedded" [38]. More accurate but computationally more costly schemes have been developed where the background atoms are treated by super-cell slab density functional theory and the embedded atoms are described by high-accuracy quantum chemistry calculations [39, 40]. Embedding techniques make accurate treatments of ground and excited states of defects in crystals or adsorbed molecules on surfaces possible.

2.3. Multi-scale modeling techniques

Multi-scale modeling involves at least two techniques, operating at different resolutions (degrees of detail) in space and/or in time. Results of the higher resolution simulation are fed into the lower resolution method. In some but not all techniques, there is a feedback from the coarser-grained, or low resolution, method to the finer-grained, or high resolution, one. The feedback changes the environment at the small-scale level and leads to adapted results at this level. The calculations at the different length scales are intimately related. When there is no feedback from the coarser level, the calculations are essentially decoupled (e.g., in the kinetic Monte Carlo method) and the calculation can be done by two separate programs. In the following, several techniques are illustrated to which the bridging of length and/or time scales is central.

The first two classes of methods are based on a finite element representation of the solid. The first class to be discussed does not use feedback from the coarser level. Methods in this class are called informed, or physics-based, finite element methods. The parameters governing the response of the material to certain interactions have been obtained by a higher resolution theory, e.g., molecular dynamics techniques based on an empirical description of the atomic interactions or from measured bulk properties. An example is the use of elastic constants to describe how a piece of material deforms due to a small force. For each finite element, the appropriate material properties are taken or interpolated from a database constructed from higher resolution theory or experiment. Then the finite element algorithm determines the result for the whole solid, based on the values obtained for each of the elements.

The quasicontinuum method is a finite element technique with feedback [31]. It was initially developed to analyze the structure of crystal defects [41]. To do this, a finite element mesh is set up for the solid, with the nodes corresponding to "representative atoms". These atoms represent a large number of atoms far away from the defect, where the variation from the ideal crystal structure is small, whereas they describe single atoms close to

the defect. The positions of other atoms are arrived at by interpolation. The total energy of the crystal is then derived from the energy contributed by each representative atom weighted by the number of atoms it represents. More accurate results are obtained if this is done in an ab initio fashion, for example, by applying density functional theory. When many atoms are involved, however, the exact quantum mechanical treatment of density functional theory has been too demanding computationally so that generally more efficient, yet less accurate, methods have been used to date, e.g., empirical interatomic potentials [41], or a semi-empirical quantum mechanical method such as a tight-binding technique [42]. The physical properties for elements in the higher resolution region are obtained by (approximately) treating the actual atomic structure. For consistency, the values in the coarse-grained region are generally computed with the same interatomic description as in the fine-grained region. One difficulty is the construction of a correct description of the boundary between the two regions. In particular, the questions of how to transport heat or mass through the boundaries have not been solved.

The concurrent coupling of length scales scheme [43,44] is an alternative to the quasicontinuum method (see Fig. 6), where tight binding is used to treat the region of the solid where highest resolution is necessary (e.g., if chemical bonds are made or broken in this region, a quantum mechanical treatment is desirable). Fig. 6 shows this region in the lowest panel. The tight binding region is coupled to a larger region described by molecular dynamics with empirical potentials (the middle panel in Fig. 6), which in turn is connected to the largest region, the rest of the solid (the upper panel in Fig. 6). It is treated by a finite element method, assuming a continuum approximation of the solid in that region. By contrast, the quasicontinuum approach treats the whole solid by a finite element method, where the properties in the elements are derived from one single method for both the representative atoms and the explicit atoms on the finest scale. Also, unlike the quasicontinuum method, the concurrent coupling of length scales technique does not offer the possibility to adapt the finite element grid after it has been set up. The
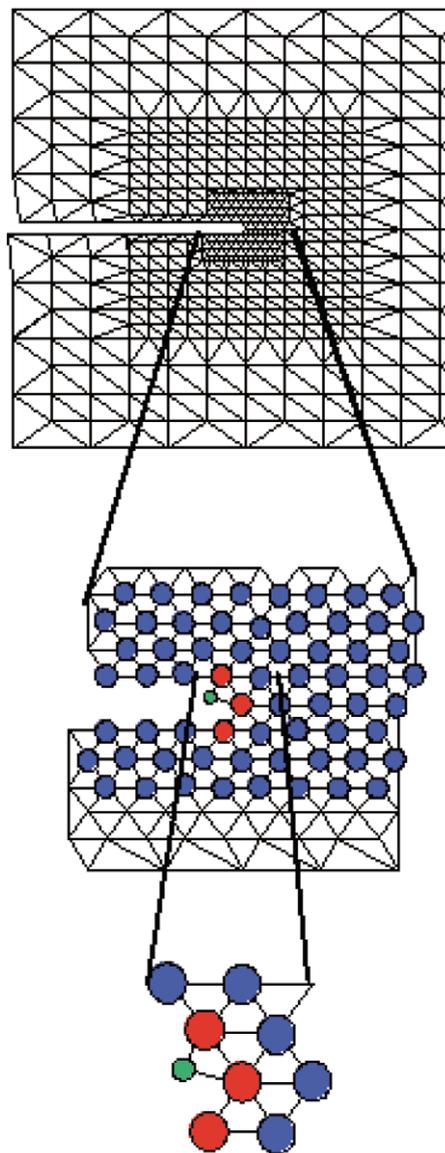

Fig. 6. The figure shows the resolution at different length scales as used in the concurrent coupling of length scales method. The largest length scale is treated by a finite element grid using the continuum approximation of the solid. Increasing the resolution, the individual atoms are considered by molecular dynamics with empirical potentials. Quantum mechanical effects are taken into account at the highest resolution using a tight-binding method. In the concurrent coupling of length scales method, the mesh refinement is defined once at the beginning. In the quasicontinuum method, the whole solid is covered by the finite element mesh, which can be adaptively refined during the simulation to atomic resolution in the region near the crack tip (courtesy of W.A. Curtin).

concurrent coupling of length scales method ensures that the total energy is conserved, however, while this is not guaranteed in the quasicontinuum approach. In the concurrent coupling of length scales method, three different algorithms are at work. They are connected at the region boundaries by appropriate ''handshaking'', making sure forces are correctly coupled across region boundaries. It is the boundary where atomic resolution and the continuum approximation meet that poses the greatest problems. To improve the situation, a replacement for the finite element part has been suggested: coarse-grained molecular dynamics [44], a scale-dependent generalization of finite elements which passes smoothly into molecular dynamics as the mesh is reduced to atomic spacing. Finally, use of tight binding in the concurrent coupling of length scales strategy makes the modeling of metals difficult in many cases; the authors of this hybrid scheme suggest that the quantum mechanical heart might be replaced by another rather inexpensive quantum mechanical method such as kinetic energy density functional techniques [45].

A different method of bridging length, but more importantly time, scales is the kinetic Monte Carlo technique. This method provides the possibility to study the evolution of a system for longer times and with more participating species than is possible by traditional molecular dynamics. Kinetic Monte Carlo is a variant of ordinary Monte Carlo, where processes have a probability of execution governed not by the Boltzmann probabilities but by ratios of rate constants that quantify how often processes happen. In some cases, elementary processes can be isolated in experiments and their rate constants measured. Alternatively, the rate constants are obtained from ab initio or from more approximate, empirical potential calculations, or left as phenomenological input variables. Once the relevant processes have been found and their rate constants obtained—not a trivial undertaking—the Monte Carlo part can begin. Some implementations (e.g. Refs. [46,47]) start with the random selection of a species and choose at random a process that is allowed for that species. Then a random number between 0 and 1 is selected by the computer and is compared to the rate constant of the process divided by the largest rate constant, the reference rate constant. If this rate constant ratio is greater than the random number, the species reacts, otherwise it is left unchanged. This means that ''faster'' processes (which have larger rate constants) happen more often. After N attempted moves, where N is the number of species, the clock is advanced. In some implementations, the time step is the inverse of the reference rate constant, corresponding to the time needed to execute the fastest process [46]. In others the time step is drawn from a specially adapted pool of time steps [48]. Another implementation of kinetic Monte Carlo [49] is based on the so-called n-fold way algorithm [50], where the probability and selection of a process to occur is given by its rate constant divided by the sum of rate constants, the ''total'' rate constant. Here, an event happens at every time step while, in the implementations mentioned earlier, the execution is conditional on the comparison of the rate constant ratio to a random number.

Kinetic Monte Carlo can simulate arbitrarily long times, depending on the rate constants involved. It works most efficiently, however, when the processes simulated happen on similar time scales. In particular, processes that are very fast (where the energy barrier, which has to be surmounted by the system to move from one state to another, is almost zero) in comparison to the others can be problematic, since then the individual time step is very short. This means that the simulation of longer time intervals is costly. To avoid this problem, one can have all species undergo the very fast processes according to their equilibrium probabilities before attempting a traditional kinetic Monte Carlo move. The very fast processes are assumed to be executed instantaneously, i.e., without incrementing the clock, and can be treated in a computationally cheaper manner [47]. In all implementations of kinetic Monte Carlo, the explicit simulation of unproductive events (i.e., events, that ultimately leave the system unchanged) is omitted, increasing its efficiency compared to molecular dynamics. Also, it is easy to change the concentration of species and to study the effect of such changes. Kinetic Monte Carlo also can predict the kinetic order, i.e., how the rate at which a reaction happens

depends on the concentration of the reactants (for an example, see Ref. [47]).

Kinetic Monte Carlo can only give an accurate rendering if all the relevant processes are known in advance, since they are inputs to the simulation. If important processes are left out, the simulation can produce qualitatively incorrect results. For example, Jónsson and co-workers found that the shape of platinum islands in simulated growth on a platinum surface can depend dramatically on the inclusion or exclusion of a single process [51]. An example of a counter-intuitive process that might have been left out of a kinetic Monte Carlo simulation is how metal atoms can diffuse on metal surfaces. It was discovered only recently that on some surfaces diffusion occurs not primarily via repeated hops on top of the surface as illustrated in Fig. 7(a), but rather by a concerted displacement in which the adatom replaces an atom in the surface layer, which in turn moves to the surface, reminiscent of the butterfly swimming style [52–54] (as displayed in Fig. 7(b)).

Another factor limiting kinetic Monte Carlo is its assumption of a complete decoupling of pro-

cesses. Like any Monte Carlo scheme, the kinetic Monte Carlo method is stochastic (random or probabilistic) by definition. Also, the way a state is reached is not taken into account and thus cannot influence the evolution of a system. The molecular dynamics method, on the other hand, is deterministic: any configuration of the system at any time step is connected by Newton's laws to the configuration at prior and subsequent times. Molecular dynamics methods also give access to properties of the system that can only be determined from a trajectory. Among these are so-called time-correlation functions, from which, e.g., vibrational spectra can be derived that reveal the motion of an atom or molecule on a surface. As another example, energy and angular distributions of colliding molecules can be predicted from gas-surface scattering events [17,18]. However, since the evolution time step is limited by the fastest motion in the system, typically an atomic vibration ($\sim 10^{-12}$ s), it only can simulate events happening on very short time scales. Rare events (those with a high energy barrier) generally do not occur during these short time intervals. If the objective is to study a rare event, though in principle it is not necessary to know the processes a priori, it is required in practice because the simulation usually cannot be run long enough for the rare event to happen unprompted. In particular, transition states—those unstable states which, if perturbed slightly, will evolve into either the initial or the final state—can be located a priori. An example of a transition state is denoted in Fig. 8(a) by a cross. One can follow the rare event of crossing a transition state by starting there, and following the molecular dynamics trajectory forwards and backwards in time to construct the entire trajectory [55,56]. A further drawback is that generally the quality of the calculation is not sufficient to study chemical reactions, with a few exceptions [4]. However, if the quality is improved by using ab initio calculations for the forces, the method is considerably slowed down, and only a few trajectories may be sampled, leading to poor statistics.

Several methods for treating longer times using variants of molecular dynamics have been developed. One can retain the advantages of traditional molecular dynamics as long as one makes
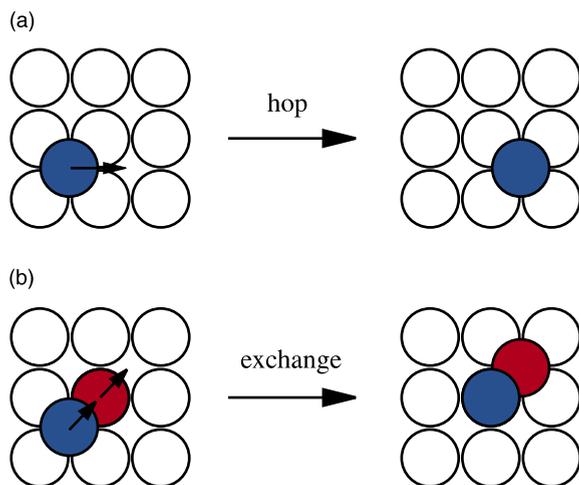

Fig. 7. Schematic illustration of two mechanisms of diffusion on a metal surface. To model diffusion in a kinetic Monte Carlo simulation, all processes likely to happen must be included in the model. The hop process shown in panel (a) is easily imagined. Some metals prefer, however, a cooperative exchange mechanism (shown in panel (b)) over the hop process [52]. (Figure after A.F. Voter, private communication.)
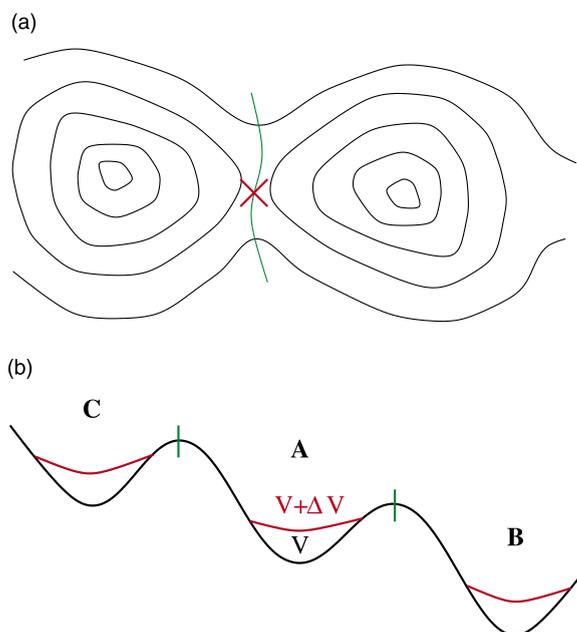
(a)

(b)

Fig. 8. Schematic representation of potential basins separated by energy barriers (the "watersheds" are denoted by green lines). Panel (a) shows a "map" view with contour lines indicating lines with the same potential height V. The transition state is the point through which the transition from one basin to the next requires the least energy. It is indicated by a red cross. In accelerated molecular dynamics [58,59], a bias potential ΔV is added to the potential V (see panel (b)) to make the potential basins shallower, leading to an extension of the time that can be simulated. (After A.F. Voter, private communication.)

the additional assumption that the system obeys transition state theory (TST) [57]. TST assumes that barrier crossings are uncorrelated and that no recrossings of barriers occur. One can then consider the evolution of a system as a sequence of infrequent transitions from one potential basin to another. (A potential basin is a region in space where the potential energy is lower than in the surrounding region, as shown in Fig. 8(a)). A system in one of these basins spends a lot of time meandering around, or vibrating, in one state, going up the potential hills in different directions, then down again, until it at some point climbs over a hill to cross through a transition state into another basin. One idea to speed up the method is to shorten the time spent in the basins. To get meaningful results, this quickening of the pace has

to be done keeping the relative probabilities of different escape routes unchanged with respect to the original system. Several approaches achieve this by artificially shallowing the potential basins [58,59], most recently the hyper-molecular dynamics method [60–62]. As depicted in Fig. 8(b), a bias potential is added to the deep potential wells, keeping the transition state potential energy unchanged. This modification preserves the ratio of the TST escape rates from basin A to any two adjacent states, since the energy barrier is lowered by the same amount for both transitions. This means that the escape to a given adjacent state (say, B) happens with the correct relative probability. The boosted time can be calculated from the time elapsed during the trajectory occurring on the biased potential surface. In cases where empirical potentials determine the forces (ab initio molecular dynamics is currently out of reach), this has led to a speed-up of up to four orders of magnitude. However, in more complicated systems, the determination of the bias potential can be cumbersome [63]. An approach which avoids the difficulty of determining the bias potential is the temperature-accelerated dynamics method [63].

3. Multi-scale modeling in surface science

A multi-scale approach to the modeling of materials is necessary whenever elementary processes taking place in a small region or a short time affect behavior on larger scales in a manner not describable by interpolation. A class of examples that does not require multi-scale modeling is the simulation of a material before and after a complete change of phase, e.g., from solid to liquid due to an increase in temperature or from one crystal structure to another due to a change in pressure. The properties of the uniform phases can be determined from the investigation of small unit cells, usually neglecting the imperfections of a real material. However, when the aim is to understand the phase transition *itself*, a look at different length scales simultaneously is a must. Atoms rearrange themselves in their immediate neighborhood, zones of different phases form within the material, complex breaking and forming of bonds—chemistry—happens at the

zone boundaries. The zones expand, needing a description at a higher length scale, while the elementary processes continue to happen at the atomic length scale. We next give examples of current and future applications in surface science that demand the use of multi-scale methods.

3.1. Surface modeling across length and time scales

Conventional single-length scale modeling can be performed at the atomic or a higher length scale. Extrapolating material properties from atomic results obtained with assumption of perfect periodicity neglects the defects and irregularities present in a real crystal. This atomic-scale-only approach is as limiting as a coarser model that includes empirical input or, worse, fitting parameters. While the latter includes large-scale effects that cannot be described on the atomic scale, an understanding of the basic reasons for the phenomenon investigated is lacking.

3.1.1. Bridging length scales

We now examine the contribution to the understanding of surface phenomena that can be achieved by combining the low-resolution continuum model with higher resolution input. Our first example is the reconstruction of crystal surfaces that occurs when a crystal is cleanly cut into pieces. "Reconstruction" refers to the rearrangement of atoms at the surface to lower their energy (bonds are broken when the surface is created, raising the energy of the surface atoms). Many theoretical approaches have been and are being used to describe surface reconstruction [64]. A multi-scale description is particularly important in cases where the reconstructed pattern (the surface unit cell) is large compared to the interatomic distance. Cammarata used an informed continuum model to describe the reconstruction of metal surfaces of two orientations [65]. Four properties of the newly created (i.e., unreconstructed) surface, among them surface tension and surface stress, were obtained from empirical embedded atom method [66] or density functional theory calculations (depending on the metal). A continuum analysis yielded an estimate for the energy difference

between the freshly cleaved and a fully relaxed surface. Simple continuum formulae model how the four quantities affect the way the surface layer contracts and how defects are formed, breaking up the original surface. A negative energy difference between the unreconstructed and the reconstructed surface indicates that energy can be released if the surface reconstructs. The authors derived a simple criterion to determine the sign of the energy difference, involving only the four quantities obtained at a higher resolution and one additional parameter. They evaluated this criterion for ten metals and can correctly predict (in most cases) which surfaces reconstruct.

The description of crystal growth requires a knowledge not only of the way atoms or molecules react on the surface (on a short time scale, with atomic resolution) but also of the way islands develop (long time scale, rougher resolution) [67]. Arrays of small islands, called quantum dots, that confine electronic motion in all three spatial directions, are being considered for a variety of applications in the electronics industry. The shape and the stability of quantum dots have been investigated in a multi-scale approach. For a quantum dot to form (rather than a film), the gain from elastic relaxation energy has to be larger than the cost of increased surface energy (the three-dimensional island has a greater surface than an equivalent two-dimensional film). The relaxation and surface energies also are the main terms in the total energy of a quantum dot. In the calculations of Pehlke et al., surface reconstructions and surface energies for different semiconductor surfaces have been calculated by density functional theory [68–70]. The surfaces are shown in the upper panel of Fig. 9. The elastic energy and the strain field (the local distortion of the lattice) can be accurately described by elasticity theory (if the island has more than one thousand atoms, as the authors find). The equilibrium shape of the island is then calculated within a finite element framework by determining the minimum of the total energy of the island with respect to its shape. Each finite element represents a part of the island and the substrate in which the atoms are similarly arranged. Taking the strain into account by modeling all the atoms would be expensive computationally,
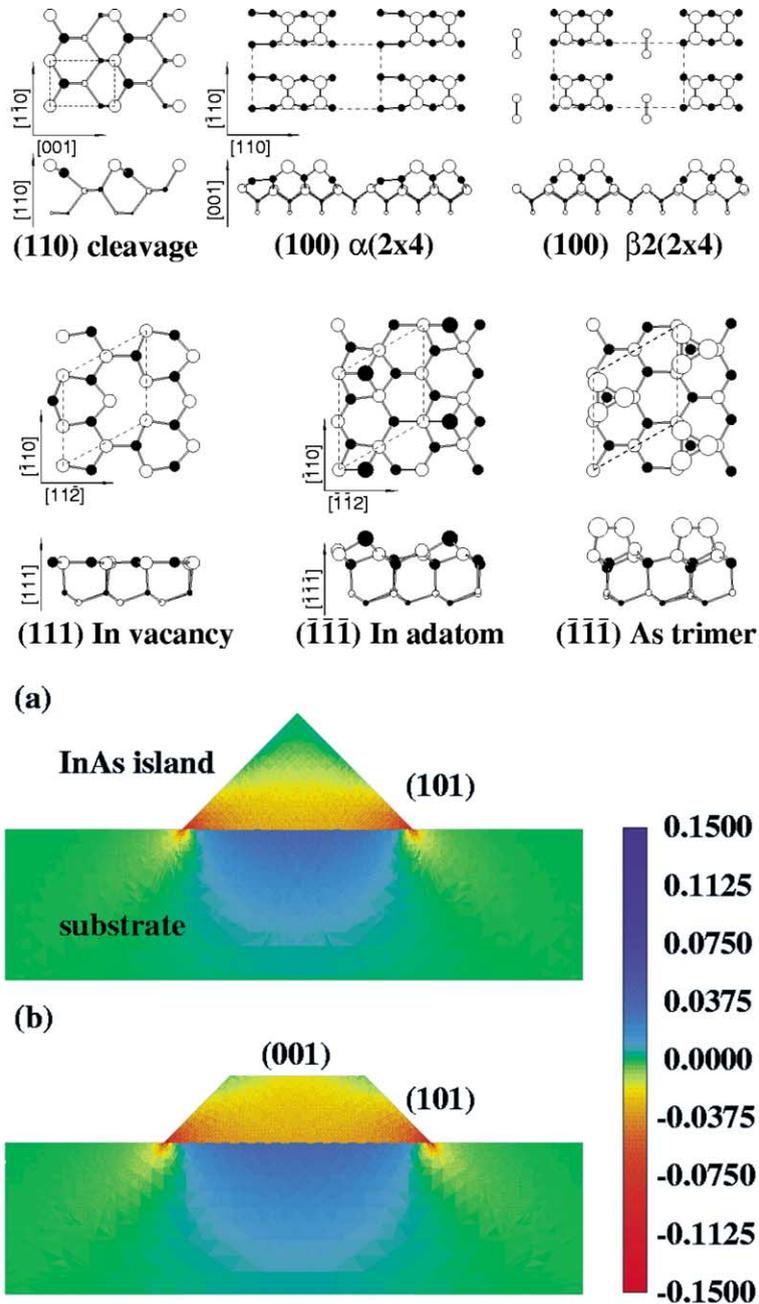
Fig. 9. Island shape determined by a multi-scale method combining ab initio calculations of surface energies and stresses with an elasticity theory description of long-range strain fields and strain relaxations. The top panel shows the surface models that were used in the quantum mechanical calculations. The lower panel shows the strain (a measure of the distortion of the crystal) for two islands of different shape and the underlying substrates. (Figure from Ref. [69], courtesy of N. Moll.)

and moreover unnecessary, since long-range strain is well described by elasticity theory. The lower panel of Fig. 9 shows the color-coded strain of the island calculated with the finite element method.

As another example of where continuum models alone or atomic representations alone are insufficient, we consider the case of so-called stress corrosion cracking of a metal. In this case, atomic level surface chemistry must be described (the usual tendency is to either ignore or guess the effect of surface chemistry in continuum mechanics models). However, considering only atomic level chemistry ignores the large length scale deformations and defects in a crystal leading to cracking. In an ongoing study on the oxidatively induced fracture of aluminum (Al), density functional theory calculations are being used to provide the forces necessary to tear the metal (and its oxidized surface) apart [71]. Aluminum oxidizes immediately when it is exposed to air, as indicated schematically in Fig. 4(a). When the metal is pulled (under tension), a crack develops, forming surfaces. The pulling is an applied force, which is called traction when it is normalized by the area on which it is felt. The distance between the two surfaces of the crack is called the separation δ. Fig. 4(b) shows a finite element mesh covering a rectangular body which has a crack, indicated by the red line drawn into the body. The part most difficult to describe is the actual point at which bonds are broken and surfaces created i.e., the crack tip. The zoom image shows that the mesh is particularly fine there. Near, and directly in front of, the crack tip, it is necessary to know how the applied traction induces strain and finally opens the crack. Density functional theory is used to calculate the traction–separation relationship for two Al (or Al_2O_3) surfaces. One such curve, displayed in Fig. 4(c), may be used as input to a finite element method-based simulation of crack development. The interior of the material is treated by elasticity theory, but the forces acting near the crack tip are taken from the atomic-scale calculations. In this way, the chemistry of bond breaking (and oxidation) is described by quantum-mechanical calculations, while the crack formation in the solid is treated by a continuum model, called the cohesive zone model [72,73]. This approach also can be used to study grain boundary embrittlement by impurities (vide infra).

To get a feeling for the dimensions and numbers involved, let us take a look at the study of crack propagation in silicon modeled using the concurrent coupling of length scales method [43]. Here, a void was opened in a thick silicon slab and a strain was imposed on the outermost boundary. The tight binding region contained several hundred atoms (the electron density is (implicitly) considered at a length scale of 10^{-10} m), the empirical potential molecular dynamics region about a million atoms (treating atomistic physics at the nm scale, 10^{-9} m), and about 250,000 nodes were used in the finite element portion of the solid (continuum mechanics at the μm scale, 10^{-6} m) [43,44]. The entire system represented about 11 million atoms. It was found that the propagating crack reached a limiting speed of 2770 m/s, equal to 85% of the Rayleigh speed, the speed that sound travels on the solid silicon surface. The importance of including atoms explicitly in the description of behavior at interfaces was highlighted further in a recent molecular dynamics study [74], which found that cracks propagating along an interface between two crystals can, under certain conditions, travel faster than the Rayleigh speed, in contradiction to results derived purely from continuum mechanics.

The quasicontinuum method has been used to investigate how large a region has to be treated atomistically in the study of crack propagation. For a body of ~500 nm edge length, Miller et al. found that continuum theory and linear elasticity theory is valid for most of the solid, except for a small region near the crack tip of only about 1 nm in radius [75]. The interaction between atoms was modeled using empirical embedded atom method potentials. This result shows that a brute force simulation, where all the atoms in the body are treated individually, is unnecessary except within ~1 nm of the region where the transformations (chemistry, defect formation, etc.) are occurring.

The quasicontinuum method has been applied to a number of problems researching the mechanical stability of crystals. One study investigated what happens when cracks encounter grain boundaries in solids [75]. Grain boundaries are found where small fragments of crystal of the same material come together but the crystal lattices do not match exactly. Depending on the situation, the grain boundary can stop (blunt) the crack or

the crack can reach the boundary and then branch, running along the boundary leading to a separation of the grains. Surface chemistry can be important here, when impurities segregate to the grain boundary. These may make the material more brittle. Again, density functional theory combined with continuum theory is needed to address both length scales; such work is in progress [76].

As shown above, we have taken the first steps toward accurate modeling of surface and interface phenomena varying in length scale by powers of ten. We next consider current methods to bridge the time scale gap between atomic motions (10^{-12} s) and materials growth (seconds or minutes).

3.1.2. Across time scales

In this arena, the main surface science problem that has attracted attention is crystal growth. Of particular interest is how to choose the process conditions to achieve specific structures. The atoms comprising newly grown layers often come from the gas phase and tend to be involved in complex interactions with the surface atoms. Kinetic Monte Carlo is a natural method to choose, since it can include atomic scale processes while overcoming the long time scales for growth. One recent application of kinetic Monte Carlo, which illustrates its versatility, used rate constants derived from embedded atom method potentials to examine nickel (Ni) growth in the presence of hydrogen (H) [77]. Here, the elementary processes exhibit time constants (the inverse of their rate constants) ranging from $\sim 10^{-9}$ s for an isolated H hop to $\sim 10^7$ s for the breaking of a Ni–Ni bond, spanning 16 orders of magnitude from the extremely fast to the very slow. There is no other method available that can span such an impressive spread in the characteristic times for various processes. The presence of small amounts of H was predicted to increase the average Ni island size, helping the Ni atoms to gather together more effectively than they would on their own. Additionally, kinetic Monte Carlo has been used in connection with rate constants from density functional theory to investigate the growth of Al on Al [49], specific chemical reactions in diamond growth (in connection with a tight binding

method) [78], and the nucleation of silver (Ag) islands on platinum [79].

In desorption of hydrogen molecules from silicon surfaces, the high accuracy of ab initio quantum chemistry calculations was exploited to calculate the rate constants for kinetic Monte Carlo [4,37,47]. This model included many surface processes, e.g., H atom diffusion, defect migration, monohydride to dihydride interconversion, etc. While the kinetics were found to be first order—in agreement with experiment—for all coverages, temperatures, and independent of the presence of steps or defects, the overall desorption rate constant was quite sensitive to the concentration of surface vacancies (missing atoms). This helped rationalize the factor of 16 range in measured desorption rate constants, as perhaps due to surface preparation differences which result in variable concentrations of vacancies. To derive these results from a molecular dynamics investigation would have been prohibitively expensive due to the range of time scales involved (from very fast adatom surface diffusion to slow molecule desorption).

As an alternative to kinetic Monte Carlo, accelerated molecular dynamics can be used with empirical potentials to explore long time scales. For example, Voter has used his hyperdynamics method with embedded atom method potentials to study the diffusion of a 10-atom Ag cluster on a Ag surface at room temperature [60]. In a simulated time of 220 μs, he observed three distinct mechanisms affecting cluster motion on the surface. The temperature-accelerated dynamics approach with embedded atom method potentials has been used to study film ripening (the evolution of an initially random surface until it settles into a stable configuration) on a copper (Cu) surface [63]. A simulation of 14 adatoms on a Cu slab with the three top layers free to move (182 moving atoms) was run for a simulated time of *several hours*. An ordinary molecular dynamics calculation with the same computational work would have only reached a time on the μs scale. The simulation showed that a compact island shape was reached after 17 min, which remained stable for hours. 48 different states were visited and about 3000 transitions occurred. Such details would not have been observed on the shorter, μs, time scale, illustrating

the power and need for accelerated molecular dynamics.

3.2. Twenty-first century modeling

Surface science has matured as a field to the point that it is now found in many arenas beyond chemistry and physics, including geology, dentistry, prosthetic medicine, and sensor technology. Likewise, the field of computational sciences has grown to the point where methods are no longer routinely used in isolation. The complex problems of the 21st century demand a battery of approaches. The maturing of both surface science and computational methods allows us to dream of understanding—and then using our knowledge to solve—important problems, where surfaces and interfaces abound. They include: inorganic–inorganic interfaces and inorganic–biological interfaces found below the Earth's surface [80], in the human body [81], and in the products of corrosion [82], as well as fluid–solid interfaces important for both gas and liquid sensors [83]. The action at these surfaces involves multiple players on multiple length and time scales. For example, bone regrowth involves transport of calcium ions (atomic scale) and adhesion of cells (100 µm) via anchor proteins (<1 µm) [81]. Gas sensors involve adsorption of molecules and transport of, e.g., oxygen, while the sensor measurements may involve mechanical deformations or electrical conductivity on the microscale [83].

In the 21st century, we expect to see multi-scale modeling become a powerful partner with experiment to discern atomic scale effects on macroscopic properties. The future is expected to bring the ability to carry out, e.g., accelerated molecular dynamics and quasicontinuum calculations with forces derived not from empirical potentials but from accurate quantum calculations. Indeed the density functional theory-quasicontinuum coupling, via orbital-free density functional theory [45], is already under development [84]. More accurate means to couple different scales should appear (and other methods already exist that we have omitted in the interest of brevity!). In the end, this should allow us to simulate surface chemistry in real time and to determine its influence on the macroworld. In what follows, we give a few examples of where we can expect multi-scale modeling to impact surface science in the near future.

A classic surface chemical reaction is the oxidation of carbon monoxide (CO) by oxygen (O_2) as catalyzed by platinum surfaces. This reaction takes place daily as part of exhaust cleanup by the catalytic converter in automobiles. While the kinetics and thermodynamics has been understood for at least two decades [85], more recently fascinating kinetic oscillations have been uncovered, which are a beautiful example of atomic scale events affecting much larger length scale phenomena. In particular, complex concentration patterns emerge on the surfaces in space and time. In some regions of the surface, the dominant species is adsorbed oxygen atoms, while in others CO prevails. A variety of striking patterns have been observed, for which several mechanisms have been postulated depending on the temperature, the amount of CO and O_2 available, and the platinum surface used [85,86]. The basic origin of these patterns is the catalytic oxidation of the adsorbed CO to carbon dioxide (CO_2) (see Fig. 3). The patterns of the surface concentrations of CO and O, that can be observed in time, are fundamentally due to: (i) CO "poisoning", where high coverages of CO inhibit the dissociative adsorption of oxygen and (ii) the slow conversion rate of CO and O to CO_2. These two effects favor a high CO coverage. The adsorption of CO changes the structure of the platinum surface, however, altering at times the adsorption rate for oxygen. This allows an oxygen layer to be established, restoring the original surface structure [87]. By contrast, an oxygen layer, once formed, does not stop CO from being adsorbed on the surface. CO thus slowly returns and expels the oxygen layer. Spatial patterns on the micron scale develop when the reactions occur at different times in different areas on the surface. So far, kinetic models of these oscillating reactions embodied rate constants obtained from experiment [86]. The local time dependence of the concentrations is obtained through (differential) equations but long-range effects are neglected, in particular, the long-range surface reconstructions. A multi-scale description might start with ab initio calculation of the rate constants needed for a

kinetic Monte Carlo simulation. Furthermore, it would go beyond the purely local description of the concentrations, taking into account size and shape of the areas (on the micron scale) where one or the other species is dominant. A two-dimensional finite element method could be combined with the kinetic Monte Carlo method to keep track of these areas. The same method could keep track of the subsurface oxygen, which is formed from the surface species, and thought to alter the surface structure [86]. This approach could yield a unified description of this complex system that may reveal more about the interplay of chemistry and structure across length scales.

An example with important industrial implications is the development of thermal barrier coatings to protect metal engine parts (e.g., in turbine engines) from the high operating temperatures (up to 1700 K) and oxidizing environment of the combustion gas mixture [88]. Such coatings could be used more generally to protect any material from harsh environments. While initial density functional theory studies characterized the strength of interfaces in thermal barrier coatings [89–91], accelerated molecular dynamics and kinetic Monte Carlo studies could help determine the interaction of gases with the thermal barrier coating, the importance of ion interdiffusion at interfaces, and the effect of heat on the mechanical stability of the coating–engine interface. Linking the density functional theory results to continuum descriptions of fracture is important for a comprehensive understanding of how and why the thermal barrier coatings fail and ultimately to the design of coatings with long lifetimes.

A promising area of high-tech research is the development of microelectromechanical systems. These are small devices of an overall size of a few millimeters, with feature sizes of a few μm. The devices have electrical and mechanical components that are combined into one unit and are designed to act as, e.g., miniature sensors, actuators, valves, or gears. In these miniaturized devices, surface effects are extremely important in every normal or unintentional contact during their operation [92]. Surface roughness needs to be minimized in order to reduce wear in moving parts. In a micromotor, roughness can lead to localized electric field con-

centrations and therefore premature breakdown. Additionally, at small length scales, the effect of friction on operation is much more dramatic than in larger elements. Exposure of microelectromechanical systems to humidity increases the friction. Several materials have been examined as structural materials or as thin film coatings to reduce friction and wear and to improve reliability and lifetime. Because of the optimization of silicon fabrication technology, these devices are typically made from silicon, followed by deposition of other materials as needed. Modeling both the production and coating procedures by density functional theory combined with accelerated molecular dynamics and kinetic Monte Carlo could help select the optimal processing strategy. Theoretical tests of proposed designs—commonly used for this purpose at larger length scales—could be used to model the element in its entirety (on the 10^{-3} m length scale), incorporating atomic-level friction (on the 10^{-10} m length scale of the electron density) as needed. Such multi-scale simulations offer a cheap possibility to customize the microelectromechanical systems for very different fields of operations. Simulations of microelectromechanical sensors for gas detection could reveal the atomic level reasons for measured changes in conductivity [83], which at this point are elusive. This is critical to development of sensors that not only are sensitive to species at the parts per billion (ppb) level and stable over a long time, but also exhibit the desired selectivity. Valuable information could be gleaned by linking the atomic scale adsorption processes to large length scale ion mobility measurements, so that sensors could be built that can discriminate between a garden-variety pesticide and a chemical warfare agent.

4. Conclusions

Multi-scale modeling methods are the key to deciphering some of the most intricate problems of surface science. The problems of materials degradation and synthesis, heterogeneous catalysis, gas sensing, liquid–solid interfaces in the body (e.g., cell adhesion) are far too complex on several different length and time scales to be treated by one

method alone. For example, using atomic resolution, even coupled with an explicit treatment of quantum mechanics, is not an option to describe the structures that are present in modern day steels at the length scale of microns. Even if all atoms could be treated individually, such a simulation would be extraordinarily wasteful. It makes much more sense to try to describe regions where atoms behave similarly on a coarser scale, and to reserve atomic resolution for those areas where large deviations from the original structure are present. Multi-scale modeling promises to contribute to a wide variety of industrial applications including coating technology and gas microsensors. Multi-scale simulations also can help solve fundamental questions of chemistry, such as the complex processes involved in the seemingly simple oxidation of carbon monoxide, that give rise to the spatio-temporal patterns displayed in Fig. 3. Many problems are treated now at a single length scale simply for lack of a better description. They will soon be within the reach of current and future multi-scale techniques. The methods discussed here, as well as ones anticipated that link accurate quantum energies and forces with higher length scale dynamics, are expected to become full-fledged partners with experiment in revealing the naked truth about surface and interface phenomena in the years to come.

Acknowledgements

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