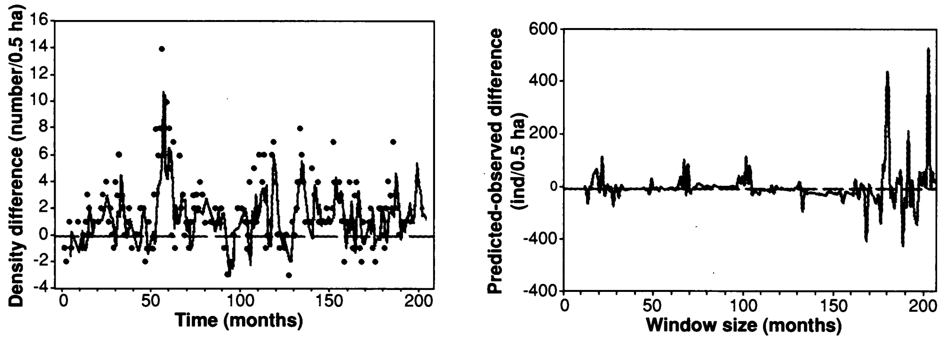

Rodents compete for seeds. (**Left**) Difference in densities of species of small rodents between plots with and without large rodents in a Chihuahuan desert ecosystem. **Actual data deviate from the model's prediction.** (**Right**) Comparison of effects of species removal actually observed and the differences predicted by a model that assumed densities could be modeled as small deviations away from average densities. Window size refers to the length of the time series used to estimate model parameters and predict densities. Average densities converge on equilibrium densities for long time series (*7*).

tive so that they will be prepared to expand upon the principle when faced with assessing the likelihood of competing complicated models.

Another critical advance needed in ecology is the adoption of a more sophisticated view of causality. Relevant processes that affect the data collected about an ecosystem often operate on different spatial and temporal scales (*11*). Accounting for the effects of such multiscale causality requires ecologists to simultaneously adopt both holistic and reductionistic perspectives on process-based explanations. In particular, many ecologically relevant process models can be described by macroscopic parameters determined by the statistical properties of many short-term, small-scale processes.

Consider the problem of predicting why the geographic range boundary for a species exists at a particular location. Relevant processes include the physiological functioning of individual organisms at the range boundary, the consequent reproductive rates of the populations that contain them, larger scale dispersal movements of individuals among populations, and geographic-scale trends in the environment. Each of these processes operates on different spatial and temporal scales. Parameters describing ecological processes at one scale are macroscopic parameters describing statistical outcomes of processes at smaller scales. For example, the birthrate of a single population is determined by the success of many individuals at obtaining and processing sufficient energy to exceed their metabolic requirements, and therefore having excess to expend on reproduction. A fruitful avenue for development of empirically relevant theory would be to frame models by using statistical mechanics designed for biological processes. Initial attempts to develop such a field have been overly simplistic, often relying on strict analogy to statistical mechanics developed from equilibrium thermodynamics.

The challenges faced by ecology have pushed the field into a new realm of endeavor, where both theoretical and empirical ecologists need to be trained in more sophisticated statistical techniques. Ecologists should be prepared to develop more complicated explanations for ecological phenomena by incorporating processes that operate at multiple scales. A lot of hard work and a little luck may ensure the emergence of an ecological science in the next millennium that will provide effective, scientifically sound tools for analyzing human impacts on the world's biological resources.

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SURFACE CHEMISTRY

Direct Imaging of Adsorbates and Precursors on Surfaces

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There can be few fields of scientific endeavor that have advanced so dramatically and contributed so much to transforming humankind's modus operandi over the second half of this century as the science of solid surfaces. Surface scientists now have at hand, for example, the remarkable immediacy of direct, real-space images of atoms and molecules at surfaces, made possible by scanning tunneling microscopy (STM). For transformations to our lifestyle we need only think of the ramifications of the transistor and the microchip industry, a technology dependent on surface preparation and processing. The present issue of *Science* contains two demonstrations of the power of STM to reveal details of dynamic processes at surfaces. On page 545, McEllistrem *et al.* (*1*) display successive snapshots of dangling bonds (unsaturated valence states) diffusing about on a silicon {100} surface, and on page 542, Brown *et al.* (*2*) report their imaging of a precursor state to benzene chemisorption on Si{111} and describe the dynamics of the transfer between states—the first direct molecular observations of a so-called (*3*) intrinsic precursor state.

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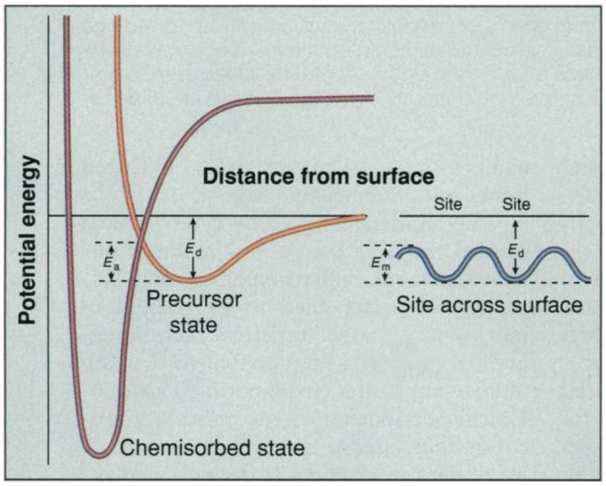
The key to many surface processes, including epitaxial growth, adsorption, desorption, and catalytic reactions, is the multidimensional potential energy surface describing (i) the arrival of a molecule at a surface, with the eventual formation of a chemical bond, and (ii) the lateral motion of the adsorbed species across the surface. Some years ago the field ion microscope was the only experimental tool available with atomic resolution, and elegant results were obtained with it for the diffusion of individual metal atoms on metal surfaces, including the collective motion of chains of adsorbed surface metal atoms (*4*, *5*). The high field (>10 V nm^{-1}) required for imaging was, however, a major limitation to the systems that could be investigated by this technique, and only with the advent of STM has it been possible to examine the diffusive motion of molecular adsorbates on surfaces by imaging individual molecular displacements. Thus, in a recent issue of *Science* Briner *et al.* (*6*) reported the diffusive behavior of carbon monoxide (CO) molecules chemisorbed on the (110) face of copper. Real-time movies of diffusive motion demonstrate that one-dimensional chains of CO molecules tend to be formed along the direction orthogonal to the close-packed atomic rows of the substrate surface and diffuse along these rows. Surprisingly these chains diffuse faster than monomeric units. For example, the hopping of a chain of seven CO molecules across the surface at 44 K was 15 times as fast as the average hopping of single molecules. This result may be ascribed to the increase in configurational entropy associated with the loss of order in a linear chain, which is a prerequisite for chain movement. The lowest energy configuration is the straight chain, due to attractive interactions between CO molecules at the inter-row distance on the substrate. An unexplained result is the very low prefactor, D_0, reported for diffusion in this work: For the motion of a monomer, Briner *et al.* report a value of 2.5×10^{-8} cm^2 s^{-1}, compared with a classical (zero-activation entropy) value of ~ 3×10^{-4} cm^2 s^{-1}. This remains a challenge for molecular dynamicists.



Surface states. A simple potential energy diagram for a molecule approaching a surface, illustrating the scheme for the formation of a chemisorbed layer through a mobile precursor state, with dissociation. [Adapted from figure 1 of (*8*)]

On the {100} face of silicon, McEllistrem *et al.* (*1*) follow the diffusive motion of empty sites within a near-saturated adsorbed layer of deuterium adatoms. These deuterium atoms form stabilized, mixed-orbital bonding states with surface silicon atoms, using the dangling bonds of the clean surface. The clean surface structure, with the top layer reconstructed to a (2 × 1) surface unit cell with silicon dimer pairs, is essentially unaltered by this process. Deuterium adatom (and hence dangling bond) diffusion is sufficiently rapid to produce a steady-state distribution of dangling bonds over a wide temperature range, and three different regimes are observed. Below 600 K the dangling bonds tend to be paired on adjacent surface silicon atoms, due to an additional attractive π-bonding interaction between these atoms. Between 600 and 620 K, paired dangling bonds still dominate, but dangling bonds on adjacent silicon dimer pairs also become occupied. Finally, at temperatures above 660 K, the dangling bonds become completely separated and the number of paired dangling bonds is substantially reduced.

There are some close parallels in these two studies (*1*, *2*), despite the fact that we are dealing with adsorbed species on the one hand and vacancies on the other. In both cases, a close dimer pair is energetically the most stable state, followed by the open configuration dimer and then the separated state. Configurational entropy also follows the same trend, increasing in the above order for both cases. In detail, however, the dynamics will reveal interesting differences. Although dangling bonds are more visible than deuterium adatoms, detailed modeling will have to take into account deuterium atom motion, including the lower vibrational entropy bridged configuration for the activated complex between sites. Conversely, in examining the interaction between CO molecules on metal surfaces attention will also need to be paid to the attractive interactions between vacant sites in this case.

The dynamics and kinetics of gas-surface interaction processes have in the past been successfully modeled by invoking intermediate or precursor states (*3*, *7*). A distinction is made between a precursor state over empty sites, known as the intrinsic state, and a state that exists over sites filled with a chemisorbed species, the extrinsic state. As reviewed elsewhere (*3*), there is spectroscopic evidence for both types, but the intrinsic precursor has proved to be rather elusive. Now Brown *et al.* (*2*) have produced direct observations of two states of adsorbed benzene at the same empty site on the {111} surface of silicon exhibiting a (7 × 7) reconstruction. The more weakly bound of these two states, stable only at low temperatures, is clearly an intrinsic precursor to the more stable chemisorbed state. Remarkably, the authors were able to use an electric field effect produced by the STM tip placed over a chemisorbed benzene molecule to switch it back into the intrinsic precursor state. The lateral diffusive motion in this state, and its conversion to the chemisorbed state, could then be monitored in detail.

These studies represent a new state of maturity in the exploitation of the scanning tunneling microscope. The development of sample temperature control is now yielding quantitative information of direct relevance to surface processes. This provides an important route to experimental benchmarks for ab initio molecular dynamics simulations of the same processes. Moreover, the field is now ripe for the direct observation of relatively complex processes and the role of surface topographical details in these processes. For all the seductive power of this technique, however, we will continue to depend heavily on the continued refinement and development of spectroscopic, crystallographic, calorimetric, and dynamic techniques, together with STM, to provide a quantitative basis for the study of solid surfaces (*8*).

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