Research News

Playing Three-Dimensional Pool

A group of chemistry "hustlers" has developed a new technique for analyzing surface structure; as one researcher says, they're "playing sticky pool with marshmallows"

THIS GAME HAS NO EIGHT BALL and no corner pockets, but anyone who has knocked a few balls around a billiards table will recognize it on sight. Nicholas Winograd is playing three-dimensional pool with individual atoms for balls and an ion source for a cue stick. But the object of the game is not to clear the table. Instead, the one who learns the most about how the balls were stacked by watching how they scatter wins.

A chemist at Pennsylvania State University in University Park, Winograd is one of only a few researchers worldwide who are using ion scattering techniques to study surface structure. Although the method is still in its infancy, during the past 2 years it has provided answers to several questions that had been difficult or impossible to get with other techniques, such as the precise distance between atoms on the surfaces of various crystals.

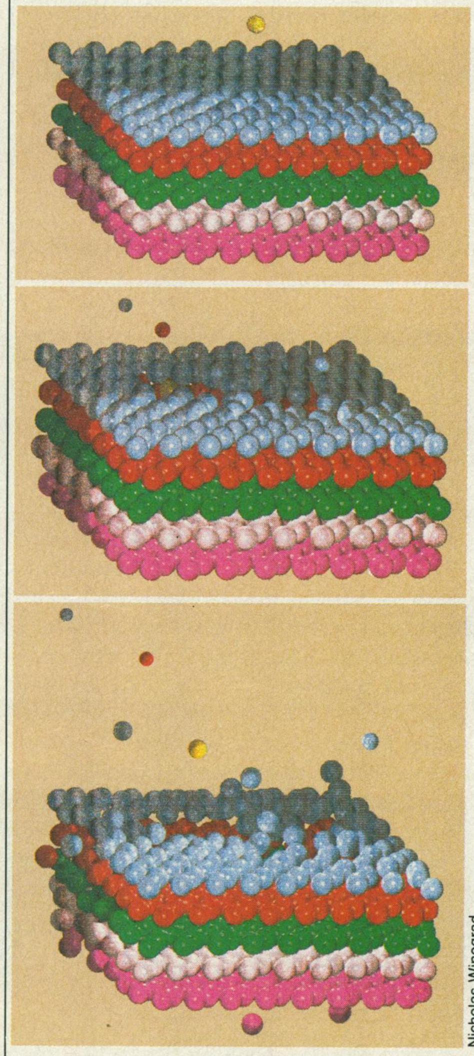
"People are just starting to realize the full potential of ion scattering," says Wayne Rabalais of the University of Houston. Eventually, researchers predict, it may be a valuable tool for such surface chemistry applications as learning how catalysts speed up chemical reactions and exploring the atomic structure of semiconductor devices.

Already, ion scattering techniques have helped Stanley Williams get details about a long-standing mystery that not even scanning tunneling microscopy—which can reveal single atoms—has been able to resolve. The chemist, whose lab is at the University of California, Los Angeles, wanted to know the exact pattern of silver atoms arranged along the surface of a crystal of silicon. The answer will offer insights into how metallic conductors couple with semiconductors, an important question in building integrated circuits.

In 1987, two groups from IBM had independently used scanning tunneling microscopes to try to determine the structure of silver on silicon (111), a particular crystalline structure of silicon. They came up with different solutions. One decided that the silver atoms arranged themselves in a honeycomb structure on top of the silicon. The other determined that the silver atoms were arranged as triplets, each topped by a silicon atom that had somehow climbed up on the silver atoms.

"I think both were wrong," Williams says. Ion scattering analysis showed that the silver atoms were in the triple structure all right, but there was no silicon on top. At about the same time, a group headed by Toshio Takahashi of the University of Tokyo used the same technique and came to the same conclusion, Williams says.

Why can ion scattering spectroscopy sometimes be effective where scanning tunneling microscopy and other surface analysis techniques are not? Although the scanning tunneling microscope can distinguish very fine details, it sees only the electron cloud around a nucleus, not the nucleus itself. In the case of the silver atoms on silicon, some unusual electronic configuration apparently confused the interpretation of the structure.



Nicholas Winograd

Atomic billiards. *When the ion (yellow) hits the crystalline target, it bounces around in the surface and knocks several atoms into space.*

Ion scattering observes the nucleus directly since the scattering is caused by the mutual repulsion between the nuclei of the incoming ions and the target atoms. As an added bonus, ion scattering can distinguish between different elements because the energy at which an ion bounces off a surface atom depends on the mass of that atom. With scanning tunneling micrographs, one can only guess about the identity of a particular atom, based on the relative sizes of the atoms in the picture and what is already known about the surface.

That ion beam techniques can give such precise structural information comes as something of a surprise. Although chemists have been firing atoms or ions at targets for decades, they generally assumed that the information obtained would be limited to a measure of the surface composition. Take secondary ion mass spectroscopy (SIMS), for instance. This is a standard laboratory method of determining which elements lie on the surface of a sample. A beam of ions knocks out atoms from the top few layers of the sample and they are identified with a mass spectrometer.

When a listener at one of Winograd's lectures heard him suggest that SIMS could be used to yield structural information, he dismissed it as "hand-grenade science." Only bits and pieces of the surface remain to be analyzed.

Nonetheless, since the 1970s, a few chemists have pursued ion scattering spectroscopy, lured by the prospect of developing a new tool to analyze surface chemistry. Their hope was that by analyzing the direction in which the "shrapnel" flew from the grenades they could get information about the geometry of the surface. They reasoned that varying the angle of the beam to the surface and watching how the number and energy of the scattered particles change should provide information about how the atoms on the surface are arranged.

It does, but that information is not easy to obtain. For one thing, the researchers have had to custom build their own pool tables. "You can't do frontline science with commercial instrumentation," Williams says. To measure the scatter of the surface particles, most of the researchers use a rather large vacuum chamber—Williams's is 12 inches in diameter and 4 feet high—surrounded by instrumentation. An ion beam fires into the chamber and strikes the target, whose angle to the beam can be set in almost any direction. The ion beams can have energies from 100 to 10,000 electron volts; 1,000 to 5,000 electron volts is most common. The detectors are of various types and are usually movable so that the angle between the beam and the detector can be changed.

But once the data is obtained, interpreting it is not nearly so simple as calculating how pool balls ricochet around a table. The researchers are shooting millions of cue balls at a time toward millions of different stacks. Winograd, for instance, uses a flux of 1 billion to 10 billion ions per square centimeter per second. And, Winograd adds, "We're really playing sticky pool with marshmallows." The complicated electronic potentials inside a solid material make it tricky to analyze exactly how the atoms bounce around when an ion strikes.

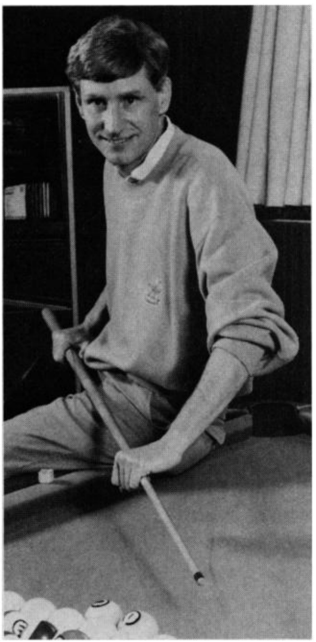
For these reasons, researchers cannot compute backward from the final state to get the original structure of the surface, as they could if the atoms were pool balls. Instead, they use models of the surface to calculate what the scattering distributions should be for different situations.

The model is as important as the data itself. It is only by comparing the data with the predictions of the model that a researcher can calculate a bond length or tell where an atom sits in relation to others on the surface.

Williams and Masakazu Aono of Japan recently developed a simple way to model what happens when an incoming ion takes one or two bounces and heads back out. Instead of considering all of the atoms in the impact area Williams looks at just two, but that is enough, he says. The model allows him to calculate the expected scattering data for a whole range of possible angles in just a few seconds of computer time, he says.

Winograd has taken a different tack. With Barbara Garrison, he has modeled the entire impact site with molecular simulations that include up to 2000 atoms. In just the past few months, he says, there has been "dramatic progress in the development of accurate force fields for modeling the dynamics of solids and surfaces." This has already allowed him to "obtain accurate descriptions of the ion/solid event, at least for a few cases."

With his detailed molecular simulations, Winograd has examined the cases where the



University Photo/Graphics, Penn State

No Fast Eddie. *But Winograd excels at atomic pool.*

The Shadow Cone Sheds Some Light

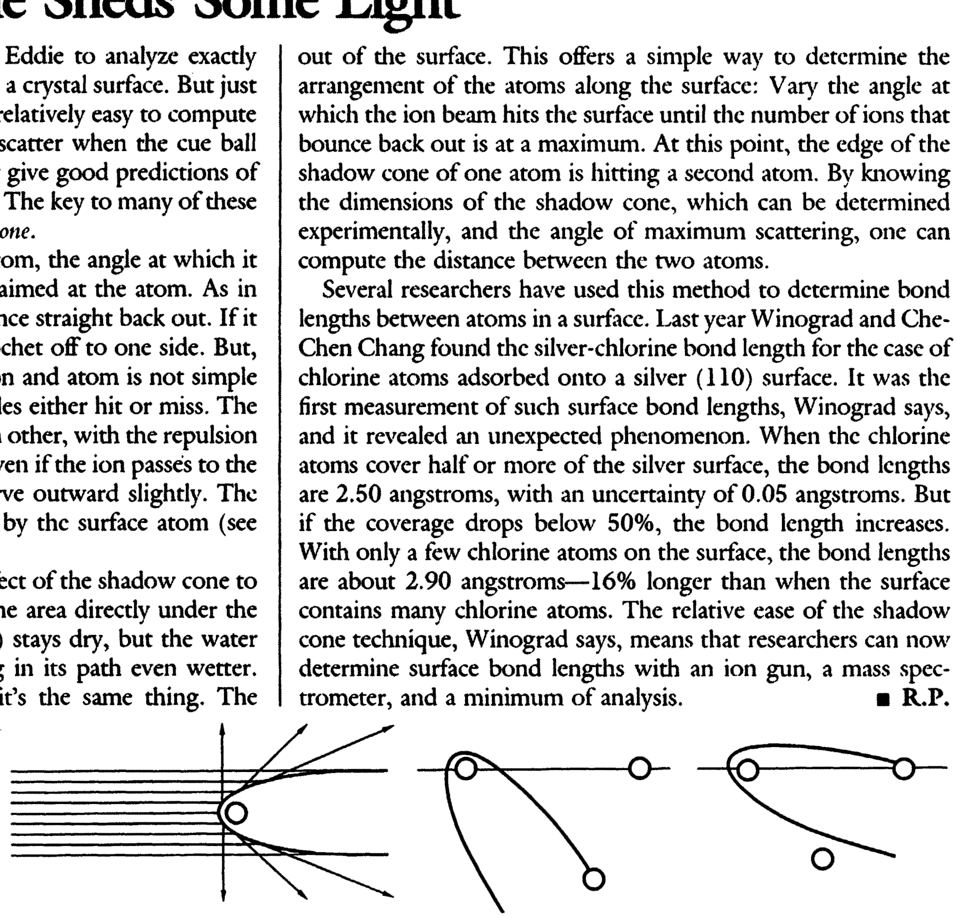
You have to be a lot faster than Fast Eddie to analyze exactly what happens when an ion crashes into a crystal surface. But just as the rules of classical physics make it relatively easy to compute where 15 "racked up" pool balls will scatter when the cue ball hits, there are some simple models that give good predictions of atom scattering upon impact by an ion. The key to many of these models is a concept called the *shadow cone*.

When an ion approaches a surface atom, the angle at which it scatters depends on how directly it is aimed at the atom. As in pool, if it comes straight in, it will bounce straight back out. If it comes in slightly off center, it will ricochet off to one side. But, unlike pool, the interaction between ion and atom is not simple elastic scattering, where the two particles either hit or miss. The two positively charged nuclei repel each other, with the repulsion getting stronger as they get closer, so even if the ion passes to the side of the atom, its path will still curve outward slightly. The result is that there is an area shielded by the surface atom (see figure). This is the shadow cone.

Nicholas Winograd compares the effect of the shadow cone to the way rain pours off an umbrella: The area directly under the umbrella (or directly behind the atom) stays dry, but the water coming off the sides makes everything in its path even wetter. When ions rain down on a crystal, it's the same thing. The shadow cones deflect the ions into certain well-defined regions off to the sides of the surface atoms.

If the edge of the shadow cone of one atom crosses the position of a second atom, then ions deflected by the first atom will hit the second one directly and recoil back out of the surface. This offers a simple way to determine the arrangement of the atoms along the surface: Vary the angle at which the ion beam hits the surface until the number of ions that bounce back out is at a maximum. At this point, the edge of the shadow cone of one atom is hitting a second atom. By knowing the dimensions of the shadow cone, which can be determined experimentally, and the angle of maximum scattering, one can compute the distance between the two atoms.

Several researchers have used this method to determine bond lengths between atoms in a surface. Last year Winograd and Che-Chen Chang found the silver-chlorine bond length for the case of chlorine atoms adsorbed onto a silver (110) surface. It was the first measurement of such surface bond lengths, Winograd says, and it revealed an unexpected phenomenon. When the chlorine atoms cover half or more of the silver surface, the bond lengths are 2.50 angstroms, with an uncertainty of 0.05 angstroms. But if the coverage drops below 50%, the bond length increases. With only a few chlorine atoms on the surface, the bond lengths are about 2.90 angstroms—16% longer than when the surface contains many chlorine atoms. The relative ease of the shadow cone technique, Winograd says, means that researchers can now determine surface bond lengths with an ion gun, a mass spectrometer, and a minimum of analysis. ■ **R.P.**



Figuring the angles. *Scattering increases when the shadow cone (left) falls across a second atom.*

cue ball burrows into the stack of other balls, knocking some of them off the surface. In such cases, Winograd has found, molecules that lie on the surface of the target are often ejected whole. Even large and fragile organic molecules can be bounced off without being broken apart, he says.

This leads to some intriguing possibilities, Winograd says. Chemists would dearly love to be able to watch what happens when a metal such as platinum catalyzes a reaction between hydrocarbons. Not only are such reactions commercially important, they are also scientifically interesting. If ion beam techniques can be improved, perhaps they will allow chemists not only to observe the intermediates in these chemical reactions but even to see which sites on the metal surface the organic molecules are binding to.

The University of Houston's Rabalais is working along these same lines. He is using direct recoil ion scattering spectroscopy to study the distribution of hydrogen on metal surfaces, which is important in understanding catalysis. "No other technique can give you this information," he says.

Rabalais recently mapped out where oxygen and hydrogen atoms attach to tungsten (211). The (211) face of a tungsten crystal has a peculiar structure of deep troughs running between high rows. Rabalais found that oxygen atoms sit inside the troughs, forming bonds with two first-layer tungsten atoms and one second-layer atom. Hydrogen atoms, on the other hand, "tend to be mobile and occupy a broad region above the troughs," he says.

Right now the field is small—Rabalais, Williams, and Winograd make up a majority of the U.S. researchers—but it is surprisingly diverse. The scientists each have their own ways of doing things, and they tend to disagree good-naturedly about which techniques are superior. Rabalais, for instance, points out that more than 99% of the particles ejected from a target are likely to be neutral, so electrostatic detectors—like Winograd and Williams use—miss most of them, while his time-of-flight detectors see them all.

Winograd, in return, has found a clever solution—using lasers to ionize the neutral secondary particles. Since the laser can be set to ionize only certain atoms, and since it will ionize nearly 100% of those, the technique is quite sensitive, Winograd says. In one experiment, he detected indium atoms adsorbed on a silicon surface with a sensitivity of 9 parts per trillion—a factor of 100 better than any previous surface analysis.

In other words, if Winograd's game were billiards instead of atomic pool, you wouldn't want him to hustle you.

■ **Robert Pool**

Galileo (Whew!) Changes Course

On 11 November, less than a month after setting out toward Jupiter, the Galileo spacecraft successfully completed its first mid-course correction maneuver—and controllers back at the Jet Propulsion Laboratory breathed a hearty sigh of relief.

And with good reason. It so happens that Galileo's 12 tiny thruster engines are susceptible to overheating—a fact discovered less than a year before the spacecraft's 18 October launch, when an identical thruster exploded on an Earth-orbiting satellite. The ones aboard Galileo were hurriedly redesigned, says Galileo mission director Neil Ausman. But for safety's sake, they are now operated only in "pulse mode": 1 second on, then several seconds off.

Galileo's course corrections have accordingly become remarkably tedious and painstaking. "By the standards of any earlier spacecraft, it's a much more complex, much more drawn out operation," Ausman concedes. It took 2000 pulses and 3 days to give Galileo a velocity change of just 17 meters per second, whereas with a spacecraft such as Voyager the whole thing could have been handled in less than 1 day.

As an added complication, says Ausman, those thruster pulses also had to be synchronized with Galileo's rotation rate of three revolutions per minute. Otherwise, the exhaust gases might have contaminated cameras and other instruments located on a section of the spacecraft that is *not* spinning. (The rotating section carries instruments that need to constantly sweep through the surrounding Jovian plasma.)

And finally, the pulses also have to be precisely timed so that they push Galileo sideways as well as forward. On earlier missions the spacecraft might have been turned so that the thrust ran conveniently along its axis. But turning a spinning spacecraft such as Galileo is a tricky business at best. And besides, Galileo is now in a situation where it cannot be turned.

The problem is that this first leg of the journey will take it by Venus, whose gravity will give the spacecraft some of the energy it needs to get out to Jupiter. But going toward Venus means going inward toward the sun, whose heat might well destroy Galileo's fragile main antenna. And that is why the spacecraft must stay resolutely pointed in one direction: it has to hold a little sunshade in position to keep its antenna safely in the shadows.

In the end, however, things went almost perfectly. Says a happy Ausman, "It was an excellent maneuver." This time around, anyway. Before Galileo arrives at Jupiter in 1995, he and his colleagues will only have to do this another 30 or so more times.

■ **M. Mitchell Waldrop**

Readers Write to Right Wrongs

Several of *Science*'s sharp-eyed readers spotted a typographical error in a news story on a new algorithm for simplifying algebraic expressions (*Science*, 15 September, p. 1190). A misplaced cube root sign changed $\sqrt{\sqrt[3]{\sqrt{5}+2}-\sqrt[3]{\sqrt{5}-2}}$, which is a grotesquely complicated way of saying 1, into $\sqrt[3]{\sqrt{\sqrt{5}+2}-\sqrt[3]{\sqrt{5}-2}}$, which solves out to about 1.129. A few readers caught a second error. The complex roots of the cubic polynomial $x^3 - 2$ are $\sqrt[3]{2}(-1 \pm \sqrt{-3})/2$, not $\sqrt[3]{2}(1 \pm \sqrt{-3})/2$.

We're proud of our readers' algebraic acuity and chagrined about the errors. We're also chagrined to have to report that the algorithm itself has been called into question. The computer scientist who developed the algorithm, Susan Landau of the University of Massachusetts at Amherst, may have made too strong a claim for it.

At a meeting of the American Mathematical Society in August, and earlier at a computer science conference, Landau claimed that her algorithm could take a complicated algebraic expression containing roots within roots—what mathematicians call nested radicals—and rewrite it in the least possible nested form.

But when she submitted her paper for publication, the referee who reviewed it spotted a technical flaw in the proof for the theorem underlying the algorithm. Landau has corrected her theorem. It now says that the result will either be in the least nested form or have, at most, one extra level of nesting. Although Landau has yet to find any algebraic expression that doesn't reduce to the least nested form when run through the algorithm, she can't prove that that will always be the case. And unless someone does, her theorem will have to hedge its bets.

■ **Barry A. Cipra**