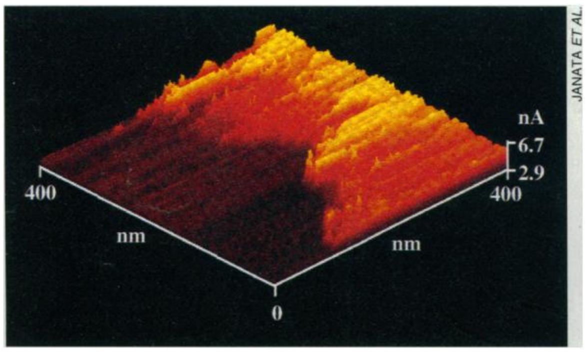
MICROSCOPY

Scanning Probe Microscopes Look Into New Territories

In the 10 years since it first showed up in the laboratory, the scanning tunnelling microscope (STM) has distinguished itself as a workhorse in the scientific instrument stable. It has been of particularly high value in research on solid states of matter; scientists use its novel ability to detect individual surface atoms and manipulate the atomic landscapes of conductive hard surfaces.

Now researchers have taken this tool into new territories. One extension is to use STMs to take an unprecedented look at the quantum mechanical behavior of electrons, behavior that changes depending on the atoms in the neighborhood. "This is a mini-breakthrough," says Joseph Stroscio, an STM researcher at the National Institutes of Standards and Technology. The technique used in these studies involves an ultrafine stylus that hovers slightly above a conductive surface and senses topographical details via tiny fluctuations in the "tunnelling current" that forms between the stylus and the surface. It allows researchers to measure quantum phenomena that had been accessible only through theoretical calculations and inference from indirect observations.

The new quantum mechanical arena is extensively described in this issue in a report on p. 218, in which STM expert Donald Eigler from IBM's Almaden Research Center in San Jose, California, and his colleagues demonstrate that STMs can directly observe changes in the quantum mechanical states of electrons confined to small patches of metal surfaces using what the researchers call "quantum corrals." These studies, as well as several similar projects by the Almaden team and others (see Perspective, p. 195), have shown how tiny structures, such as the minuscule ring of iron atoms shown on the cover of this issue—formed by dragging the atoms into place with an STM tip—can alter the quantum mechanical setting on the surface to make electrons behave like standing waves, a phenomenon not directly observed before.



Liquid up close. This image from a scanning tunnelling microscope shows a plateau of organic molecules rising above the smoother surface of a mercury drop.

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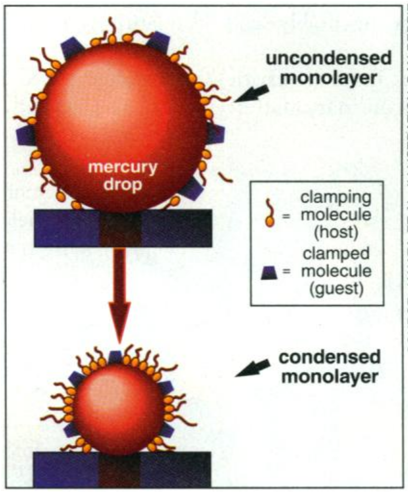
Yet these productive forays are not the only new ventures being undertaken with STM technology. Some of these ventures take the instruments out of the familiar territory of solid states and onto unknown liquid surfaces. This August, for instance, Jiri Janata of Battelle's Pacific Northwest Laboratory (PNL) in Richland, Washington, told a meeting of the American Chemical Society that he and his colleagues had trained an STM on a drop of mercury and on some molecular samples on the surface of the drops. This is the first time a report of an STM has been used to study liquid surfaces, whose mobile atoms would seem to complicate such probing, Janata says.



Molecular vise. As a mercury drop shrinks at the end of a syringe, foreign molecules on its surface crowd together in an immobilized mass, fit for study by a scanning tunnelling microscope.

SOURCE: JANATA ET AL. ILLUSTRATION: DAN REBEIZ

"A lot of work is going on with conventional surfaces [such as metal and semiconductor crystals], but this is new and intriguing," concurs Robert Nowak, manager of the electrochemical sciences program for the Office of Naval Research, which funds Janata's work. The experiments work because of mercury's extremely high surface tension, which makes the drop's surface cohesive, and because mercury is conductive, which is a criterion for any STM substrate.

One aim of this research is to turn the mercury surface into a "molecular vice" for clamping sample molecules in place as an STM scans from above. To create the vice, researchers draw the sample-coated drop back from the tip of a mercury-filled syringe, causing the drop's surface area to shrink. With less surface space, the sample molecules also squeeze together. Like a sparse crowd suddenly packing tightly together, the molecules become immobilized long enough for an STM to get a look at them.

Confirming that the "vice" is really working, Janata's group offers images suggestive of patches of organic molecules clamped in place on a mercury drop's surface in a forthcoming issue of the surface science journal *Langmuir*. If their work is borne out by others, it could open up the possibility of using an STM to probe atomic-scale details of the interface between two liquid phases, Nowak says. In this case the fluid phases are mercury and a fluid-like film of organic molecules, but other such interactions include nutrients passing across cell membranes and organic contaminants infiltrating groundwater, and the ability to image them could be quite valuable.

Janata notes that his technique could reveal molecular details about the way toxic contaminants move between two liquids that don't mix together, like oil and water. That information, in turn, could ultimately aid efforts to clean subterranean lakes of hazardous organic fluids in contact with groundwater. PNL is partly funded by the Department of Energy precisely to grapple with such conundrums. Before they are able to clean up anything, however, the researchers need to develop techniques for imaging fluids that resemble the environment of hazardous wastes more closely than does mercury.

Another, more fundamental goal is to develop a "stochastic" surface whose atoms move around more than the surface atoms of a solid substrate material like copper or graphite. That way, Janata says, the structure of the sample molecules wouldn't be influenced by the rigid structural order of a solid substrate, and researchers presumably would get a picture of the sample that's closer to reality. Work on solid substrates yields gorgeous images, Nowak adds, "but you can be fooled by preconceptions."

Researchers seem to be quite pleased with these new territories microscopy is carving out, and sometimes they are surprised as well. Scientists at the Nutrasweet Company's Research and Development Center now use an atomic force microscope (AFM), an STM cousin designed to probe biological samples, to examine how particles of a fat-substitute affect the texture of cheese. Says Steven Chastain, Nutrasweet's AFM champion: "These instruments are so hot now that you have to follow them day to day."

–Ivan Amato