be extrapolated from the average density of about 0.1 fm^{-3} found in ^{208}Pb to the 0.3–0.6 fm^{-3} of neutron stars, but the situation might not be so straightforward. For example, the material could undergo a phase transition. Superfluid and superconducting phases are thought to exist inside neutron stars, but the phases' dynamics are poorly understood. Some researchers have speculated that the environment could support a fluid of deconfined quarks or even host hyperons, which are baryons that contain the usually unstable strange quark.

Tighter constraint

A more precise measurement of the neutron-skin thickness would help clarify the connection between atomic nuclei and neutron stars, but PREX has reached its limit. There's no way PREX could get an entire year of run time at Jefferson Lab, which is what it would need to appreciably improve its measurement precision. A new dedicated facility in Germany, the Mainz Radius Experiment (MREX), is its planned successor. In addition to enjoying longer run times, MREX will be able to capture and isolate elastically scattered electrons at a higher rate using a purpose-built spectrometer.

With its targeted design, MREX is expected to shrink the uncertainty of the ^{208}Pb neutron-skin-thickness measurement by a factor of two. But, according to Paschke, the experiment's start is likely at least five years away. In the meantime, the NICER and LIGO–Virgo collaborations will continue generating data to inform evolving models, and theorists have their work cut out for them.

Christine Middleton

References

1. S. Abrahamyan et al. (PREX collaboration), *Phys. Rev. Lett.* **108**, 112502 (2012).
2. D. Adhikari et al. (PREX collaboration), *Phys. Rev. Lett.* **126**, 172502 (2021).
3. B. T. Reed et al., *Phys. Rev. Lett.* **126**, 172503 (2021).
4. M. C. Miller et al., *Astrophys. J. Lett.* **887**, L24 (2019).
5. B. P. Abbott et al. (LIGO Scientific Collaboration and Virgo collaboration), *Phys. Rev. Lett.* **121**, 161101 (2018).

A microscope for measuring surface acidity

An atomic tug-of-war offers a rare insight into the chemistry of complex environments.

Atoms and molecules, the invisible building blocks of everything around us, quickly become complicated as their size and numbers increase. A molecule of just two atoms can occupy any of a multitude of rotational, vibrational, and electronic quantum states, each with potentially different behavior in a chemical reaction. With lasers and molecular beams, physical chemists can prepare and probe many of those states individually and thus dissect the dynamics of a gas-phase molecular reaction in exquisite detail.

But when a reaction takes place on a solid surface—a common scenario in industrial catalysis, materials science, and geology—it's much more of a black box. Because every atom on a rough, irregular surface is situated a little bit differently, they can have dramatically different reactivities, even to the point of steering the reaction toward different sets of products (see PHYSICS TODAY, September 2018, page 17).

Those chemical distinctions among surface sites are extremely difficult to assess directly. Experiments usually measure only the average reaction output for the whole surface; they can't readily track individual reactant molecules to see where on the surface they reacted. Re-

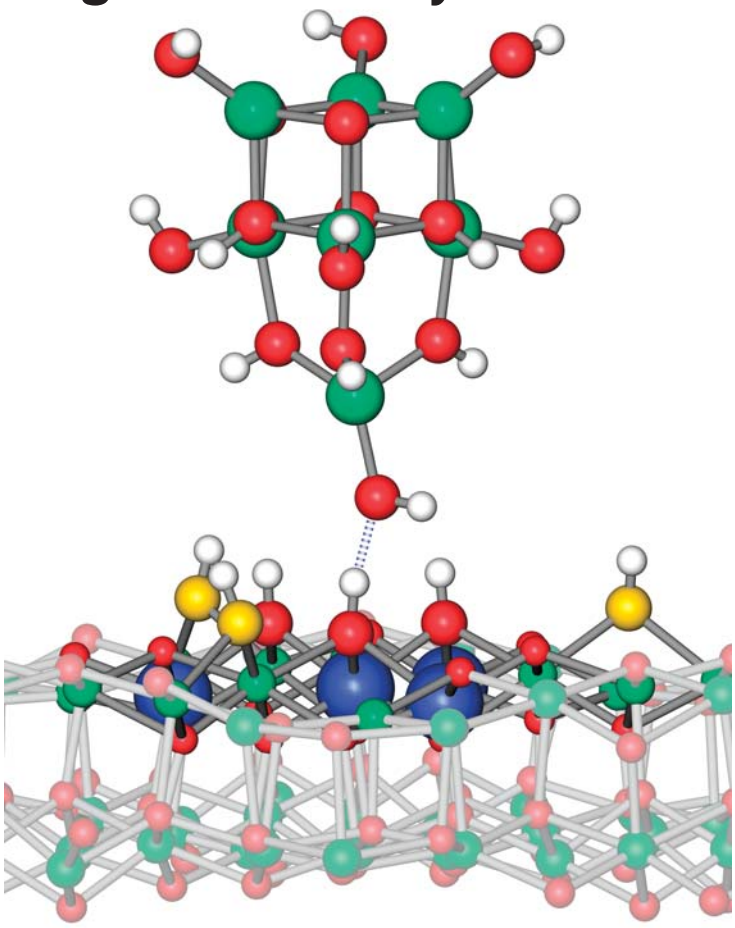

FIGURE 1. ACIDITY MICROSCOPE. When an atomic force microscope tip made of hydroxylated indium oxide descends toward a surface of the same material, the oxygen atom at the end of the tip feels an attractive force (dotted line) to a hydrogen atom on the surface below it. The force is related to the surface site's acidity: how readily it releases its H atom in a chemical reaction. Indium atoms are shown in green and blue, O atoms from adsorbed water in yellow, other O atoms in red, and H atoms in white. (Adapted from ref. 1.)

searchers are therefore limited in their ability to rationally design new solid catalysts, counteract corrosion on metal surfaces, and understand the weathering of rocks and minerals.

Now the Technical University of Vienna's Ulrike Diebold, her postdoc Margareta Wagner, and their colleagues have adapted an atomic force microscope (AFM) to map a surface chemical property—proton affinity, otherwise known as acidity—with atomic resolution.[1]

Acid–base chemistry—the transfer of an H^+ ion from one molecule or surface site to another—is a fundamental feature of many reactions, and surface reactions are no exception. (For just one example, in the catalytic cracking of hydrocarbons, a solid catalyst needs to transfer protons from its surface to fill out the newly severed C–C bonds.) By separately measuring how readily each site attracts and releases protons, the researchers offer an unprecedented look at the sites' respective roles in such a reaction.

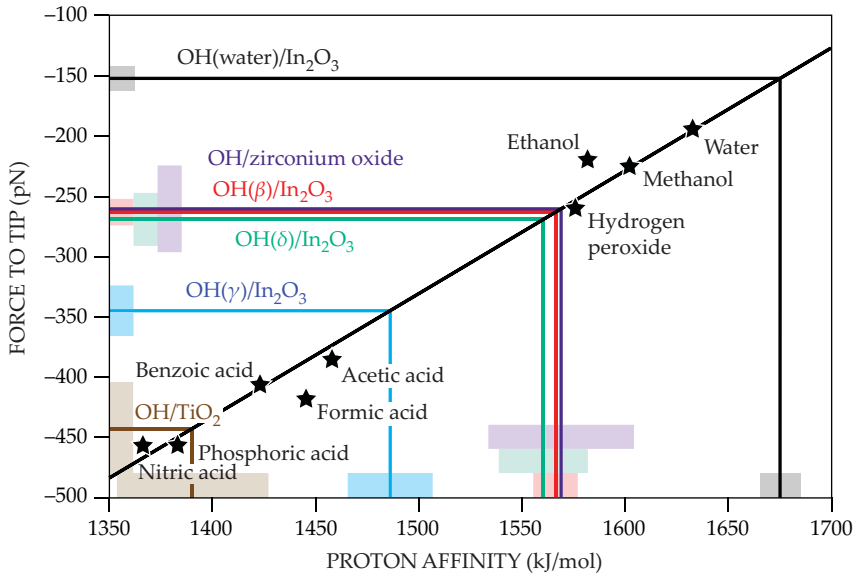

FIGURE 2. THE QUANTITATIVE RELATIONSHIP between proton affinity and atomic-force-microscopy (AFM) forces is derived from a series of density functional theory calculations on molecules of known acidity (black stars). The best-fit calibration line can then be used to convert measured AFM forces to proton affinities for surface sites. So far, proton affinities have been found for three oxygen sites on indium oxide (red, green, and blue), water adsorbed on indium oxide (black), and oxygen sites on zirconium oxide (purple) and titanium dioxide (brown). The shaded blocks represent the surface measurements' error bars. (Adapted from ref. 1.)

Oxygen sites

Like many discoveries, the work grew out of research with a much different initial direction. Diebold, Wagner, and colleagues were studying water adsorption on surfaces of indium oxide. When doped with tin, In_2O_3 has the valuable combination of optical transparency and electrical conductivity, so it's commonly used to make the top electrodes in solar cells and liquid-crystal displays. In its undoped form, it's a transparent semiconductor used in some types of coatings. The Vienna researchers wanted to explore whether or how the material's properties change when H_2O clings to its surface.

Given its simple chemical formula, In_2O_3 has a surprisingly complicated structure. Each O atom is surrounded by four In atoms, but all four of those O–In bonds have different lengths. At a crystal surface, O atoms can occupy four geometrically (and potentially chemically) distinct sites—denoted by α, β, γ, and δ—depending on which of the four bonds is missing. Furthermore, some surface In atoms are surrounded by six O atoms, just as they are in the bulk, and some are surrounded by five.

In previous work, Diebold and colleagues observed[2] that when a molecule of H_2O sticks to the In_2O_3 surface, it breaks apart into OH and H. The OH situates itself atop the oxide surface, with the O atom bridging two of the fivefold-coordinated In atoms and the H protruding upward. The split-off H then binds to a neighboring O atom on the oxide surface, which happens to always be one of the β sites.

The OH from the water molecule pokes higher above the surface than the OH on the β oxide site. "Initially we wanted to know if we could see the height difference with our AFM," says Wagner. "That does not sound very spectacular, I admit." But then they noticed something odd. The forces between the AFM tip and the OH differed markedly for the two types of OH site. For the water OH, the maximum force of attraction felt by the tip was around 150 pN; for the β oxide OH, it reached more than 250 pN.

When the researchers used the AFM tip to nudge the H atoms to different oxide O sites, they found that those sites, too, had their own characteristic attractions to the tip: 270 pN for an OH on a δ site, almost 350 pN for one on a γ site. (The α site proved too difficult to access and wasn't part of their analysis.)

What's more, those values were surprisingly reproducible, even across different experiments that used different AFM tips. "Usually, the chemical makeup of a tip—the atom or atoms at the tip's apex that interact with the surface—is a big unknown in techniques like this, unless you functionalize the tip on purpose," explains Wagner. "And chemically different tips can result in forces that differ by a factor of 2 to 10." The tips appeared to be chemically identical, even though the researchers weren't doing anything special to ensure that they were.

From forces to acidity

To find out what was going on, the experimenters turned to Bernd Meyer, a theorist at Friedrich–Alexander University Erlangen–Nuremberg. With density functional theory, Meyer calculated the forces between the OH groups on the surface and several hypothetical model AFM tips.

The best match to the experimental results came from a model tip, shown in figure 1, made of hydroxylated In_2O_3—the same material as the surface. In retrospect, it made sense: Tip-preparation procedures often end up transferring some material from the surface onto the tip, and the experimenters always prepared their tip over the In_2O_3 surface. "And it turned out to be the perfect tip for these experiments," says Diebold. "Once we realized that, we prepared the tip that way deliberately."

As figure 1 shows, the In_2O_3 tip has an OH group dangling from the end. As the

O atom on the tip approaches a surface-bound H atom, the two experience an attractive force, represented by the dotted line in the figure. The attraction sets up a tug-of-war for the H atom between the tip and the surface.

The tip always loses the battle: The terminal O atom already has one H atom bound to it, so the attraction it feels to a second H is weaker than the chemical bond holding the H to the surface. In fact, the more strongly the H clings to the surface O atom, the more weakly it's attracted to the tip.

To relate the AFM force measurements to conventional notions of acidity, Meyer had the idea to calculate the force between the model tip and the H atoms of a suite of small molecules whose acidities are known. From those calculations, he derived a linear calibration, shown in figure 2, that relates the AFM force to proton affinity—how strongly each molecule holds on to its H atom rather than releasing it as an H^+ ion into the surrounding solution. A more attractive (that is, more negative) force to the AFM tip corresponds to a lower proton affinity and thus a higher acidity: All the molecules with "acid" in their names are clustered in the lower left corner of the figure.

The calibration line makes it possible to convert the measured AFM forces on a surface to proton affinities for each surface site. The water OH site, as plotted in black, is the least acidic site on the In_2O_3 surface; the γ site, as plotted in blue, is the most. Using the same In_2O_3 AFM tips, the researchers have begun extending their measurements to other surfaces, including titanium dioxide (brown) and zirconium oxide (purple).

So far they've studied only regular surfaces with just one or a few types of surface O sites. Eventually, though, they want to look at surfaces with steps, defects, and impurities to see how those features affect surface chemistry. "The next big open challenge," says Diebold, "is to do all the same measurements in liquid water."

Johanna Miller

References

1. M. Wagner et al., *Nature* **592**, 722 (2021).
2. M. Wagner et al., *ACS Nano* **11**, 11531 (2017).

Macroscopic systems can be controllably entangled and limitlessly measured

Two oscillating membranes demonstrate correlations forbidden by classical physics.

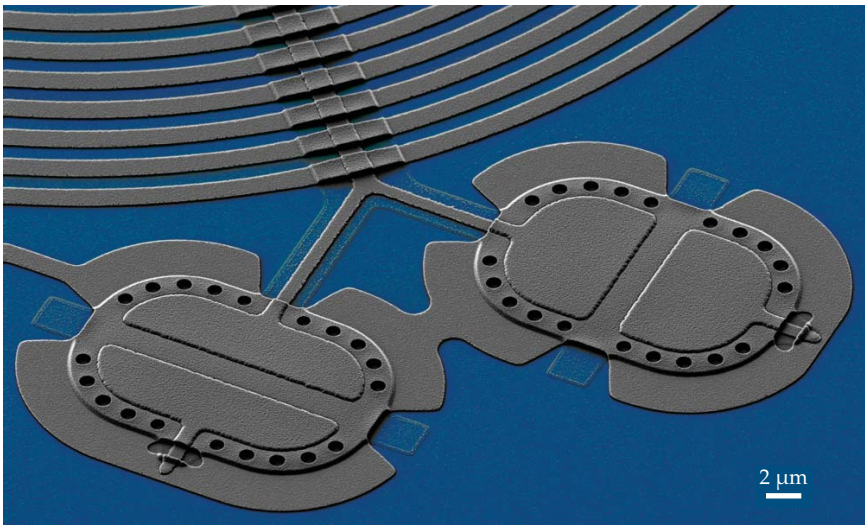

FIGURE 1. ALUMINUM DRUM membranes suspended above a sapphire substrate vibrate in a direction perpendicular to it. Each membrane forms the top plate of a capacitor, while the bottom plate is fixed to the substrate. A spiral inductor links the capacitors to form a microwave cavity. Radiation pressure from microwave pulses that impinge on the cavity drives the two membranes' oscillations to an entangled state. (Image courtesy of Florent Lecocq and Shlomi Kotler/NIST.)

What Albert Einstein skeptically referred to as "spooky action at a distance" has turned out to be one of the most important drivers of quantum technology. That spooky action, or entanglement, describes a phenomenon in which measuring the state of one particle instantaneously generates effects on another particle. The entangled particles' measurable properties are so strongly correlated that the relationship can't, statistically, have happened by chance or be explained by classical physics.

Although quantum effects are most easily observed in tiny objects, quantum mechanics is not limited to the atomic scale. In principle, objects of all sizes should behave according to quantum mechanics. But at the macroscale, quantum effects are all but impossible to detect because of limits of modern measurement tools and the tendency of larger objects to interact with noisy environments.

To bridge the gap between our daily classical experience and our expectation that quantum mechanics is universally valid, experimentalists seek quantum phenomena on larger systems. Pushing the envelope on systems in which quantum effects are observable could eventually reveal whether quantum theory does have a physical boundary.

Two research groups now report direct verification of macroscopic quantum effects that cannot be described by classical physics. In one paper, Shlomi Kotler, now at the Hebrew University of Jerusalem, and his colleagues at NIST in Boulder, Colorado, deterministically generated and directly measured the correlations needed to verify entanglement between separate macroscale mechanical objects.[1] In the other, Laure Mercier de Lépinay and her colleagues at Aalto University in Finland developed a similar system in which they could make quantum measurements that appeared to be at odds with fundamental limits associated with the Heisenberg uncertainty principle.[2]