PHYSICS

How metals dance

Observed for the first time on the smallest scale possible, an alloy of gold and silver reveals unexpected behavior in atoms

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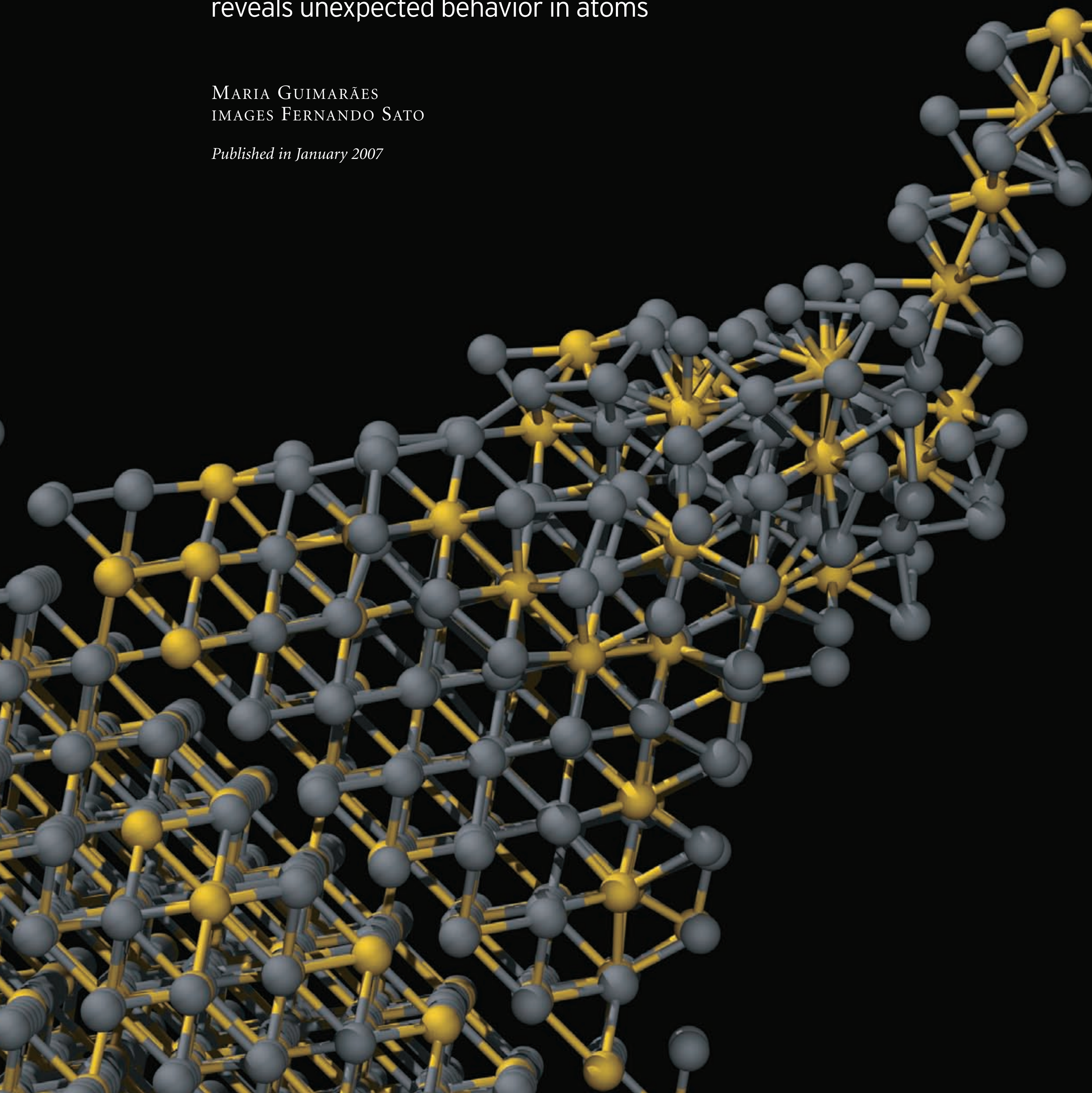
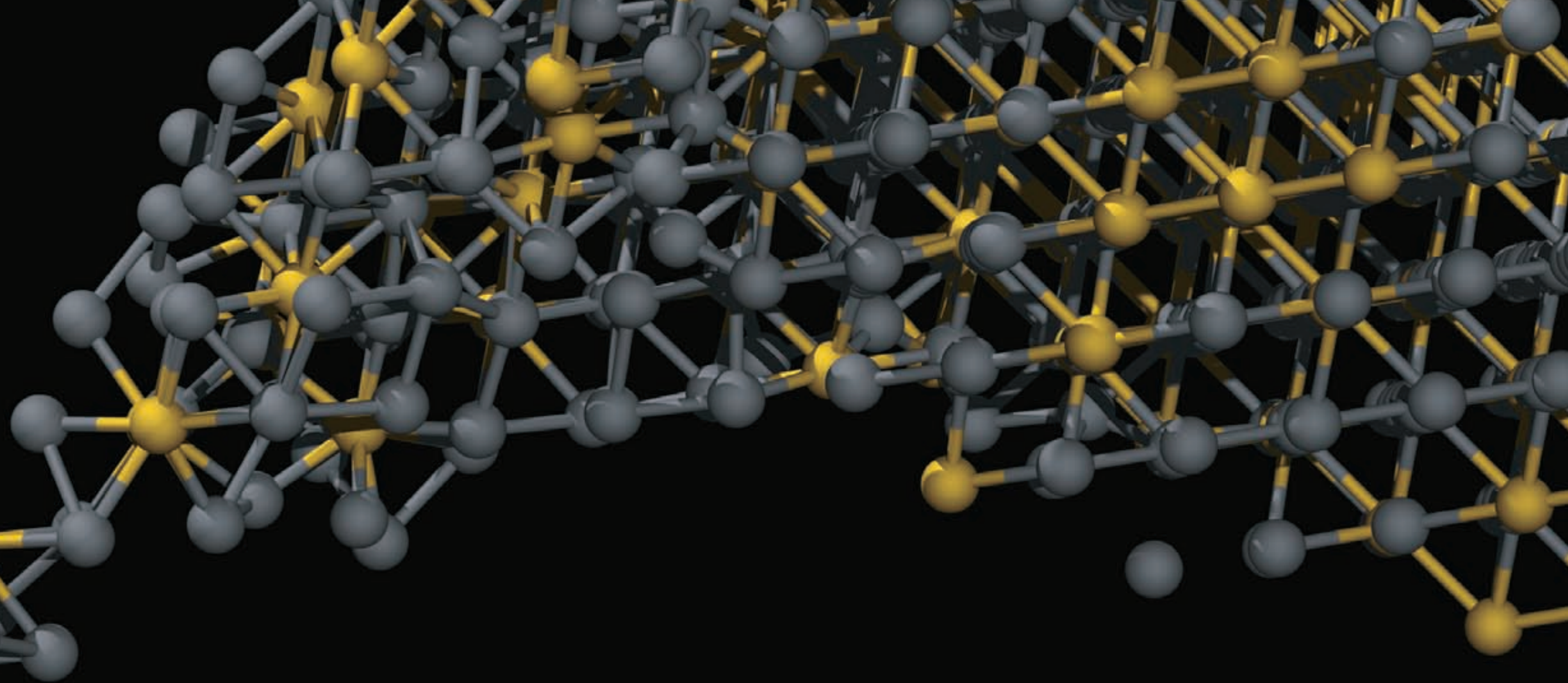
Published in January 2007





Science and art: simulations show how bonds between atoms are formed and are broken

An extremely fine layer of gold and silver pulled and stretched at the ends, becomes very fine in the middle until it can get no thinner and breaks. Observed in an electron microscope, this image in movement, which recalls melted cheese as it stretches from the bite to the ham and cheese sandwich, has nothing banal about it. It reveals what happens with such a layer at the level of the atoms, the units that make up matter. As the layer is stretched out, the bonds between the atoms burst and others form, in a snake-like dance, until a thread only one atom thick remains. These atoms lined up one by one look like a pearl necklace – a tiny ephemeral necklace, made up of three atoms, which lasts only three seconds.

Daniel Ugarte, an experimental physicist from the State University of Campinas (Unicamp) and from the National Synchrotron Light Laboratory (LNLS), in Campinas, is one of the few who have had the privilege of observing such a rare and fleeting phenomenon. His collaboration with the group of theoretical physicists led by Douglas Galvão, also from Unicamp, is responsible for great advances in the study of how metals behave on the nanometric scale, of a millionth of a millimeter. It is only after the workings of materials on this scale are understood that it will be possible to use them for technological purposes.

Ugarte and Galvão already knew that gold and silver in their pure state behave in a different way just before breaking. Both can form a wire with the thickness of one atom – or suspended atomic chains – when pulled in different directions specific for each metal. Recently, Galvão and his doctoral student Fernando Sato, in collaboration with Pablo Coura and Sócrates Dantas, from the Federal University of Juiz de Fora, explored new frontiers by simulating the behavior of the gold and silver alloys on a computer, with varied proportions of the two metals. When he saw the results, Ugarte noticed something intriguing: in a good number of the cases, the alloy would behave like pure gold. The theoretical team then went back to analyze their animations and saw that the atoms of gold migrate to the region that keeps getting thinner in the stretched metal, instead of remaining spread out homogeneously over the metal leaf. The suspended atomic chain thus almost contains only gold. "It is only when it constitutes at least 80% of the alloy that silver begins to express its properties", says Ugarte, who with his colleagues reported these unexpected results in the December issue of the *Nature Nanotechnology* journal.

Molecules in detail: computer reveals what escapes the microscope

Theory and practice - The collaboration between Ugarte and Galvão began in 2001 and involves the rare union between theoretical and experimental minds, besides tools that make a complete investigation possible, such as computer simulations, microscopy, crystallography and measurement of the transport of electric current. Each one of these techniques makes it possible to investigate a different aspect of these structures that are so small: the image in the microscope shows the moving atoms , but does not distinguish with certainty the gold atoms from the silver atoms; crystallography describes the special conformation of the atoms, but gives no information about the material's electrical transport properties. It is the agreement between the results obtained by the different areas and instruments that gives strength to the team's discoveries and discloses what an isolated look could not manage to distinguish.

As metallic alloys do not behave like pure metals, studying mixtures brings new developments that may in future help to make electronics a reality on the molecular scale . The greatest challenge to the production of alloys is imposed by the atomic properties of the materials, which, if they are very different, prevent a harmonious fit among the atoms. Sato explains that a good relationship between metals depends on the distance between two atoms in the pure metal, which is specific for each element. As the atoms of gold and silver organize themselves at similar distances, the alloy that unites these two metals is stable and easier to create, and in some proportions – such as three atoms of gold to one of silver – can even exist spontaneously in nature.

Another unexpected observation in the simulations of Galvão and Sato was the structure that appears in the images on these pages. If the alloy contains less than 10% of gold, atoms of silver organize themselves into pentagons around the gold atoms, forming a gold thread covered by silver that may work like a common electrical cable, on a scale millions of times smaller. By being a better conductor of electricity than the copper in common wire, gold is used in wire when high quality electrical transport is necessary.

For offering greater resistance to the transport of electrons, silver works as an insulator in the structure discovered by the theoretical physicists. For the time being, this structure is merely theoretical, since it arose in computer simulations and has not yet been observed in reality, but Galvão is optimistic. "As up until now the experimental results have confirmed the theoretical suppositions, the chance of the structure in pentagons existing is in fact 95%." If the discovery is confirmed, it may be an important finding for molecular electronics.

Previous experiments had already investigated the behavior of the atomic components of metallic alloys, but Jefferson Bettini, from the LNLS, was one of the first to observe it under the microscope in real time. Another advance is that the experiments were done at room temperature, which has only become possible in the last ten years, when Varlei Rodrigues, studying for a master's degree, developed a device that, with ultra-high vacuum, creates ultra-clean conditions in the environment where breaks in the extremely thin metal plates are produced. The vacuum is important because the environment has to be perfectly clean, since any intruding atom can alter the composition of the metal being studied. In general, this degree of cleanliness is attained when carrying out experiments at temperatures between minus 260 and minus 270º Celsius, which, according to Ugarte, do not lead to satisfactory results, because the temperature also affects the properties of the metal. "At such low temperatures, all materials look the same", he explains. Videos that record the breaking up of metal at room temperature and in liquid nitrogen show that the cold metal does not redo its bonds in such a dynamic way as when at room temperature. In these conditions, the process is slower, less fluid, and less representative of the day-to-day. "If a cell phone is made with nanowires, it will have to work at room temperature", he argues.

The case of the metal nanowires is a good example of how nanoscience is still at an exploratory stage, since the migration of the atoms of gold to the spot of the break and the structures in a pentagon that protect the gold wire were completely unexpected reactions. Furthermore, Ugarte explains, "on the atomic scale, objects are tacky". A nanowire suffers a spontaneous attraction for the substrate on which it is supported, like an exacerbated force of gravity, which makes manipulation difficult. But doctoral student Denise Nakabayashi has developed an apparatus that makes it possible to manipulate wires of 1 micron (one thousandth of a millimeter).

Most of the applications of nanotechnology are yet to come. According to Galvão, 80% of what is done in this area is still at the stage of understanding how metals work on the nanometric scale, practical applications to be considered next. He believes that nanotechnology is still between ten and 15 years away from being part of the day-to-day. Galvão presumes that even if the suspended atomic chains normally do not last more than a few seconds, constructing stable nanowires will not be a problem: you just have to use another material as a support. The difficulty lies in constructing wires with a known composition, in an effective and controlled manner. One option is to use synthetic molecules like the Lander, constructed in 2002 by Danish and French researchers, and is so called as it looks like a lunar exploration module.

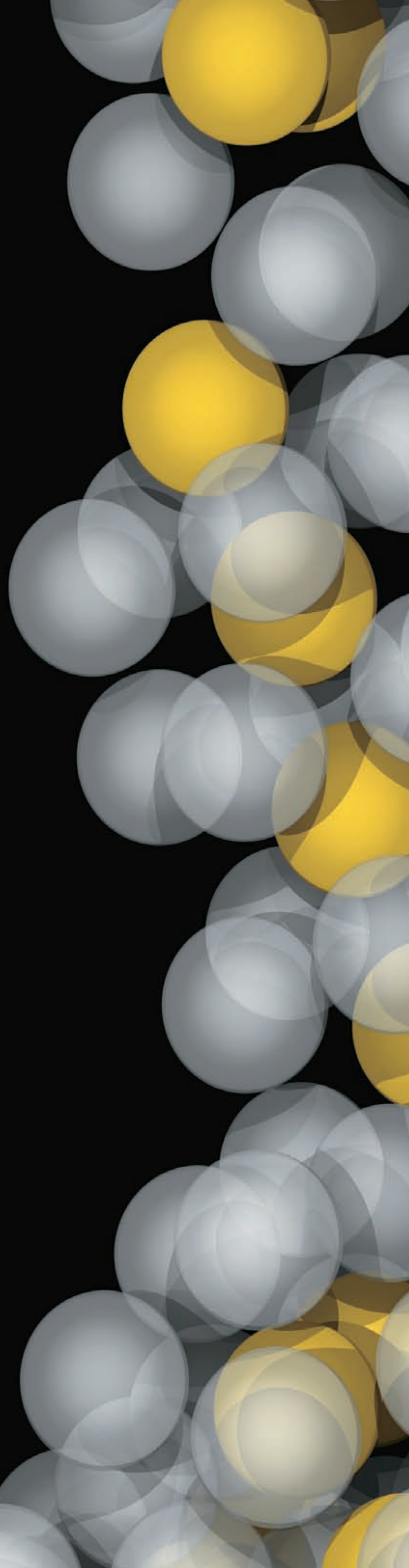
It is made up of atoms of carbon and hydrogen – a long axis with lateral projections that work like paws. Galvão and Sato explained, with simulations published in 2004 in the *Nature Materials* journal, how the Lander molecule goes for a walk amongst loose atoms and leaves behind it small lengths of copper nanowires. To construct other nanomaterials, made to measure molecules may be very useful. But Galvão stresses that many of these kinds of discoveries happen by chance. "Luck favors them, but the eyes have to be ready to see."

But when – and if – the technical obstacles and the obstacles in knowledge are overcome, nanocircuits may change electronics a lot. Not only for their size, which would make it possible to manufacture much smaller apparatuses, but also for their properties. On the nanometric scale, the conducting of electricity does not follow the same rules of the macroscopic world. In nanowires, the energy comes in packets, instead of being continuous as in the sockets of a house. But the transmission is efficient, despite being inconstant. And energy is not dissipated, according to Ugarte, which would mean electrical circuits that do not heat up.

In spite of relatively little still being known about the atomic behavior of material, the knowledge that exists, coupled with human imagination, has already made it possible to create a large quantity of products that may brighten up the Christmas of technology fans. The page on the Internet of Project on Emerging Nanotechnologies (www.nanotechproject.org) brings a list of over 300 of them, which include everything from carbon nanotubes for flat monitor screens to silver nanoparticles that fight bacteria and mold in food packaging.

The high technology necessary for studying atoms is costly, and for this reason Ugarte's projects have astronomical budgets – an electron microscope can cost from R$ 3 million to R$ 7 million. This work requires special installations that make a new building necessary – the construction of which the physicist is coordinating at the LNLS. But, for him, what limits the advance of experimental nanoscience is not the financial resources, but human resources. It is common for his pupils to have to do a master's degree course to construct or learn how to use a piece of equipment, and finally to be able to apply it to research in doctorate studies , as Varlei Rodrigues and Denise Nakabayashi did.

"You can't get people who like DIY: you have to understand, to think, to have patience, to get the measurements wrong. The students are used to finding immediate answers on the Internet", observes Ugarte, who is doing his bit to change this picture. The same principles that guide him in the academic education of his pupils, Ugarte adopts at home. His children Pedro and Maia, 6 and 4 years old, make homemade macaroni, go down hills in a soapbox car made at home, and they have now constructed a telescope in partnership with their father. ■



THE PROJECTS

Multiscale theoretical study of pure and hybrid nanostructures

MODALITY
Thematic Project

COORDINATOR
Marília J. Caldas - USP

INVESTMENT
US$ 85.268,00 and
R$ 181.110,54 (FAPESP)

Analytical transmission electron microscope for spectroscopic nanocharacterization of materials

MODALITY
Research Grant - Regular

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Daniel Ugarte - Lnls

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US$ 2.500.000 (FAPESP)