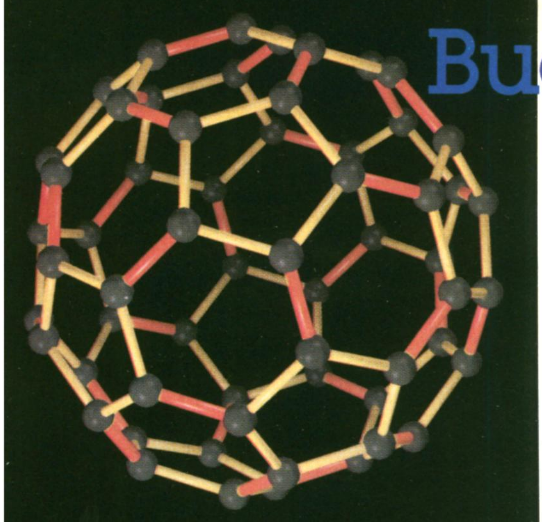
Buckyballs Still Charm

Scientists ponder the surprising properties of C_{60} and its siblings

By ELIZABETH PENNISI



Buckyball's single (yellow) and double bonds (pink) link 60 carbon atoms.

Palmer/NC Supercomputing Center

Many children will remember 1991 as the year of the turtle – specifically the Ninja Turtle, which has popped up in movies, games, T-shirts, songs, watches, even popsicles.

But for research chemists, 1991 is the year of the buckyball.

Ever since scientists figured out last year how to make these 60-carbon spheres in large enough quantities to study and manipulate, buckyballs have piqued the curiosity and imagination of those seeking building blocks for new materials. Moreover, the symmetry and other properties of this unusual molecule make it an intriguing model for understanding how atoms work.

Scientists have flooded the journals with new results as buckyballs, or "buckminsterfullerenes" – members of a family of all-carbon molecules called fullerenes – undergo every conceivable experimental and theoretical study. In recent months, investigators have shifted from examining the structure of C_{60} itself to seeing how the molecule operates as part of a solid. Some chemists have tried substituting its carbons with other elements. Others have made "fulleranes" and "fullerites" – compounds combining the carbon spheres with other substances – and then studied the properties of the resulting materials.

"We must make as complete a picture as possible," says Karoly Holczer, a solid-state physicist at the University of California, Los Angeles.

The more they discover, the more researchers wonder whether there's anything fullerenes cannot do. These molecules seem capable of withstanding great pressure and trapping foreign atoms inside their network of carbons. In July, scientists added magnetism to the buckyball's list of talents. This month, two groups announced that buckyballs also show great potential as a nonlinear optical material (see story, p.127). And new data about another surprising property, superconductivity, have convinced some researchers that they may be close to understanding how this organic material can let electrons flow so easily when combined with potassium, rubidium or other elements. Others say they have saturated buckyballs with fluorine atoms; still others have learned some of the secrets of controlling chemical reactions involving fullerenes.

The symmetric buckyball's 60 atoms fit together so well that the molecule exhibits properties that make it seem like one giant "superatom," says Richard E. Smalley, a chemist at Rice University in Houston and one of the molecule's biggest fans. He emphasizes "super" not only because of C_{60}'s remarkable versatility – it reacts with many substances and maintains its integrity under a variety of conditions – but also because the buckyball is bigger than any true atom by several orders of magnitude.

Though fullerenes resemble aromatic (ringed) carbon compounds in some aspects of their structure, chemists continue to uncover surprising differences in their properties. "It's not your run-of-the-mill organic molecule," notes Mark M. Ross of the Naval Research Laboratory in Washington, D.C. "There will be significant new materials that will come out of this, but this is so broad, I don't know where it will stop."

Along with new materials will come new insights into how atoms behave. Often, weak attractions called van der Waals forces try to keep some materials together as liquids or solids, but at room temperature, the atoms and molecules pack in so much kinetic energy that they break the weak bonds. Buckyballs also bond in this way, but their large size makes for attractions strong enough to hold these "superatoms" together as a solid even at room temperature. "And because it is bigger, it lets you do scanning tunneling microscopy," says John H. Weaver, a materials scientist at the University of Minnesota in Minneapolis. "You can image for the first time a van der Waals solid. That's something that is quite new and quite interesting."

Viewed as an atom rather than a molecule, the buckyball "represents an intermediate scale between the atomic and macroscopic [levels]," adds Holczer. "This provides the possibility to study collective phenomena at a very different spacing. It will deeply influence the way we see and understand these phenomena. The knowledge we gain will be used everywhere in every other material."

So far, buckyballs have demonstrated two unexpected capabilities: magnetism and superconductivity. The magnetic property emerged in experiments led by Pierre-Marc Allemand at the University of California, Santa Barbara. In the July 19 SCIENCE, he and his colleagues describe a compound they made by combining buckyballs with a reactant that readily donated its electrons to the carbon molecules. They cooled the material and then warmed it, and discovered to their surprise that it became magnetic after it warmed to 16 kelvins. Only one organic magnet works at a higher temperature (SN: 7/6/91, p.15).

This finding came on the heels of reports of superconducting buckyball films that worked at ever-higher temperatures, and was followed by a report of buckyball compounds that remain superconducting at temperatures as high as 45 kelvins (SN: 8/10/91, p.84).

It seems that the ability to conduct electricity without resistance arises whenever each of the buckyballs gets hold of three extra electrons, say Holczer and physical chemist Robert L. Whetten of UCLA. The critical temperature – the highest temperature at which the material remains superconducting – relates to the spacing between buckyballs.

Because potassium, rubidium and cesium represent successively larger atoms, each of these "dopants" increases the distance between the buckyballs a little more and should likewise increase the compound's maximum superconducting temperature, scientists suggest. Despite the large difference in their critical temperatures, potassium-doped and rubidium-doped buckyballs "are amazingly similar" in their physical properties, says Whetten, who has just finished experiments examining these properties.

Studies of doped buckyballs under high pressure support the sizing role of inserted atoms. Physicists Joe D. Thompson and Günter Sparn at the Los Alamos (N.M.) National Laboratory subjected the potassium-buckyball superconductor to a pressure of 21,000 atmospheres. In the June 28 SCIENCE, they report that the material's critical temperature under such pressure was 11 kelvins lower than that of a sample at ambient pressure (1 atmosphere).

Usually, pressure compresses the atoms in a superconductor, thereby allowing the electric current to move freely at higher temperatures, says Sparn. But by putting a rubidium-doped buckyball under pressure, "you can easily bring the critical temperature down to the same level as potassium [buckyballs]," adds Whetten, who collaborated with the Los Alamos group on this work. The only difference is that at normal pressures, rubidium pushes the buckyballs slightly farther apart than does potassium.

Imaging studies add to scientists' understanding of superconductivity in buckyballs. These experiments confirm that three atoms fit comfortably around a buckyball, but more than three will distort the buckyball lattice, causing the conductive properties to disappear.

In the June 20 NATURE, physicists describe the structure of the three-potassium superconducting buckyball, based on X-ray diffraction. As predicted, the buckyballs arrange as corners of a cube, with an extra carbon molecule in the face of each cube. The potassium fits neatly in spaces between buckyballs, (see diagram, p.121), says Peter W. Stephens of the State University of New York at Stony Brook, who led the research effort.

A similar scenario plays out under a scanning tunneling microscope. In the July 26 SCIENCE, investigators report that when a buckyball material contains more than three potassium atoms per carbon sphere, it becomes nonmetallic and its structure becomes distorted. Materials scientist Yun Zhong Li and his co-workers at the University of Minnesota in Minneapolis, working with collaborators from Rice University, found that extra potassium seemed to disturb the buckyball lattice, perhaps shifting the buckyballs out of the faces of the cubes.

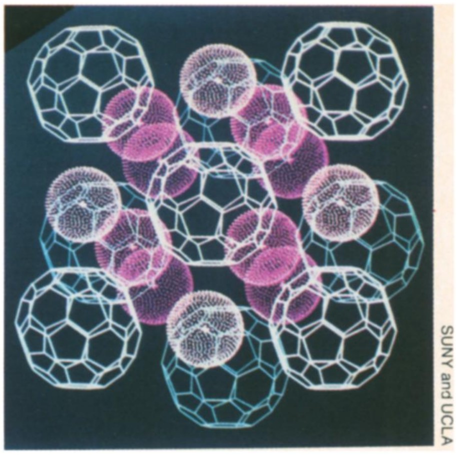
Robert Fleming of AT&T Bell Laboratories in Murray Hill, N.J., and a separate team led by Otto Zhou at the University of Pennsylvania in Philadelphia have verified that the arrangement of buckyballs changes when six potassium atoms crowd each buckyball (SN: 6/8/91, p.358).

A few scientists think buckyball superconductors will never amount to much and that the fullerene family's allure will soon fade, but others say they have only begun to tap its potential. "I know a lot of people think its popularity must have crested, but I don't think so," says Whetten. "The big challenges are really not yet solved."

He predicts that researchers will eventually serve up buckyballs a hundred different ways, polymerized and with distinctive chemical "flavors" resulting from additions to the buckyball molecule, substitutions in the carbon network itself or "guest" atoms and molecules trapped inside the carbon spheres. "But these are tough problems," he adds.

Fred Wudl, an organic chemist at the University of California, Santa Barbara, echoes Whetten's cautious optimism. In April, Wudl and his colleagues discovered how easily buckyballs – each of which has six reactive sites – react with other substances. Now, he says, "we're learning the hard way that it's pretty difficult to put only one or two things on [a buckyball]."

Most chemists think such control is critical to exploiting a new substance's chemical potential. In the next few months, however, Wudl expects to publish new findings on how to modify the carbon sphere one active site at a time. "That will literally open up the chemistry of buckyballs," he says.


SUNY and UCLA

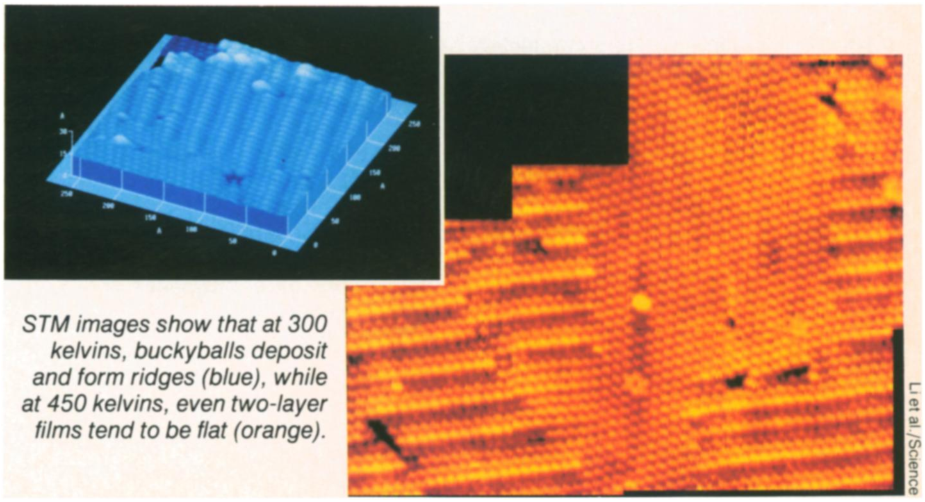
Potassium atoms, "fuzzy" pink or white, fit in between carbon spheres in a cubic buckyball lattice.

Chemists seeking to make hydrocarbon compounds containing buckyballs also seem a bit bogged down. Using computer models, Navy theorists and Yale University chemist Martin Saunders have assessed the stability of buckyballs with atoms – such as hydrogen – attached to the outside or the inside of the sphere. It seems that 60 hydrogen atoms would not fit neatly onto the outside of the carbon sphere, but would instead strain the bonds between the carbons. Attaching just one of those hydrogen atoms on the inside would reduce the molecule's energy by 10 percent, Saunders reports in the July 19 SCIENCE.

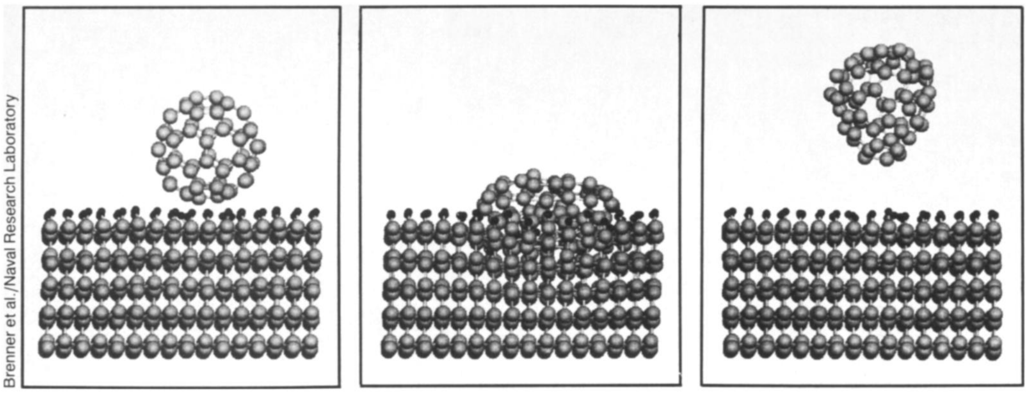
"It not only improves the structure locally, but also increases the curvature," he says. "It's like a little dimple."

His simulations suggest that shoving in 10 hydrogen atoms yields the most stable form of the fully hydrogenated buckyball, with about 25 percent of the energy of the all-outside form, he says. But those 10 atoms need to be in specific places to avoid crowding each other. "When you get two dimples too close, you get the same problems as when [the hydrogen atoms] are all outside," Saunders says. So far no one has made an inside-out hydrocarbon buckyball.

Although chemical companies have taken notice of C_{60}, "they still can't make it on the scale chemical and drug companies need to make this stuff," notes Robert C. Haddon, a chemist at Bell Labs. How-


STM images show that at 300 kelvins, buckyballs deposit and form ridges (blue), while at 450 kelvins, even two-layer films tend to be flat (orange).

Li et al./Science



Brenner et al./Naval Research Laboratory

SMASH! A simulation of the 60-carbon molecule colliding with a diamond coated with hydrogen atoms. The buckyball hits the diamond traveling at 8.2 km/sec. Both the surface and the sphere distort but then return to their original shapes.

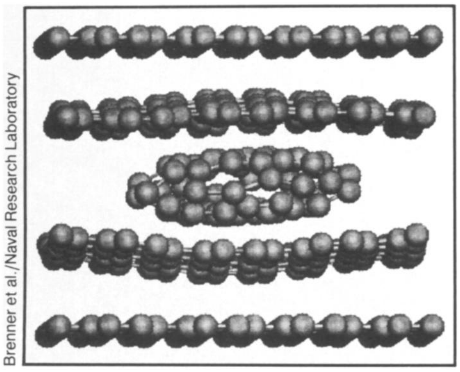
ever, researchers have made recent progress toward that goal.

Many fullerene makers have concentrated on improving their yields during vaporization of graphite rods — the standard procedure for producing buckyballs and their carbon siblings. But a group of chemical engineers led by Jack B. Howard at the Massachusetts Institute of Technology took a different route: burning benzene to make soot. Using a modified combustion chamber, they varied the pressure, fuel rate and combustion components in several experiments. They collected the soot and vapors produced over periods of about one to three hours and determined that they did produce fullerenes.

Howard and his co-workers found that C_{60} and C_{70} molecules represented up to 9 percent of the soot mass, and they say they got more of the larger fullerenes than other investigators had in the past. That yield falls short of the maximum fullerene yields of 14 percent from vaporization, but because the MIT technique lends itself more readily to scaling up, Howard and others see it as a possible way to make large quantities of fullerenes. In the July 11 NATURE, the MIT researchers note that fullerene yields increased as they increased the temperature and decreased the pressure.

Neither scientists nor chemical companies know exactly what they will do with large amounts of buckyballs, but they have lots of ideas.

For one, buckyball superconductors offer several practical advantages over other types of superconductors. Because these spherical carbon molecules conduct electricity equally well in all directions, engineers may be able to shape them into technologically useful materials more easily than other superconductors, says Haddon. Buckyball compounds may also surpass their competitors in terms of critical current density, or the amount of current the superconductor can carry before losing zero resistance. Measurements and calculations of critical current densities by the UCLA and Bell Labs teams indicate that buckyball compounds "are better than or close to the high-temperature superconductors," Holczer says.



Brenner et al./Naval Research Laboratory

Computer simulation shows a buckyball compressed to one-third its radius. It does regain its shape when released.

Other chemists want to harness C_{60} as a lubricant that may work even better than graphite. "It's like curved graphite," says Donald W. Brenner, a theoretical chemist at the Naval Research Laboratory. "It doesn't have any edges, and that's a good thing." At the Navy lab, theorists have used computer models to predict how buckyballs respond to squashing. In their simulation, they applied very large pressures to buckyballs sandwiched between two sheets of graphite, compressing the molecules to less than half their original diameter. And the buckyballs still bounced back. "It's very resilient," says Brenner, who took part in the study. The group now plans to look at how the carbon spheres respond to shear forces — being rolled and squashed all at once.

In addition, the Navy theorists have explored how buckyballs would behave in collisions with solids or gases — calculating, for instance, the impact on each carbon atom when the sphere crashes against a diamond. Their computer models suggest that buckyballs, unlike most other molecules, don't fall apart but instead bounce off intact. Experimental results support those conclusions, says Richard C. Mowrey, a research chemist at the lab. At the very least, C_{60} might work as a molecular shock absorber, Brenner adds.

Wudl expresses uncertainty about C_{60}'s potential as a lubricant. He notes that buckyballs attract one another and thus may be unlikely to flow over and past one another easily.

To circumvent this problem, chemists want to surround the carbon spheres with fluorine atoms so that buckyballs would act a lot like Teflon. Henry H. Selig from Hebrew University in Jerusalem and his colleagues at the University of Pennsylvania describe progress toward a fluorinated buckyball in the July 3 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY. Initially they obtained a mixture of yellow and tan powders, which Selig sorted by hand under a microscope. "The lighter the color, the higher the fluorination," he says. Each color still contained buckyballs with varying numbers of fluorine atoms attached, but none had as many as 60 fluorine atoms.

Chemists at Leicester University in England have had better luck making the elusive fully fluorinated buckyball. Over a period of 12 days, John H. Holloway and his colleagues heated buckyballs in fluorine gas and watched the carbon-black buckyballs transform as they latched on to more fluorine atoms. The reaction formed a dark brown material that paled to a lighter brown a week into the experiment and finally lost its color altogether. The scientists extracted material at each step of the transformation and used nuclear magnetic resonance spectroscopy to determine the ratio of carbon to fluorine atoms. The spectra indicated that $C_{60}F_{60}$ had formed, they report in the July 15 CHEMICAL COMMUNICATIONS.

Other researchers are pursuing more exotic applications: using fullerenes as molecular cages to hold other materials or modifying them by substituting other atoms for the carbons in these cages. Smalley says he is convinced that he has succeeded in getting boron atoms to replace a few carbon atoms in buckyballs, although he hasn't yet obtained enough of the material to prove his success. In experiments conducted this month, however, he may have stumbled across a way not only to substitute up to six boron atoms for carbons on the buckyball shell, but also to insert a potassium atom into the sphere at the same time. "We now think we can make lots [of this material]," Smalley says. "If it's right, it is very big."

At the Naval Research Laboratory, what started out as a routine investigation of buckyball properties has yielded results that bring chemists a step closer to putting atoms inside buckyballs. Ross had bombarded fullerenes with inert substances such as helium to break the molecules apart, and used mass spectrometry to analyze the fragments. Then, at a meeting in May, he learned that bombardment experiments by Helmut Schwarz at the Technical University of Berlin had yielded a strange result: The helium sometimes seemed to latch on to — and perhaps get inside — the buckyball. In most bombardment experiments, helium atoms hit their targets with tremendous speed and rarely stick.

"I sat and listened and couldn't believe it," Ross recalls. He and co-worker John H. Callahan went back to their lab, tried the experiments with a different type of spectrometer, and got the same results as Schwarz. To determine whether the helium was inside or outside, they bombarded the buckyball-helium molecules with high-speed xenon atoms. If the helium attached itself to the outside of the fullerene, the team reasoned, the xenon atoms would knock the helium off. But they didn't.

"This is not direct proof that the helium is inside the ball, but it's very difficult to rationalize that it is *not* inside the ball," Ross says. His colleagues at the Navy lab worked through the theoretical calculations and concluded that energized helium could punch through a buckyball if it missed or glanced off a carbon atom going in, but then hit one on the back side, slowing down enough to get trapped inside the buckyball.

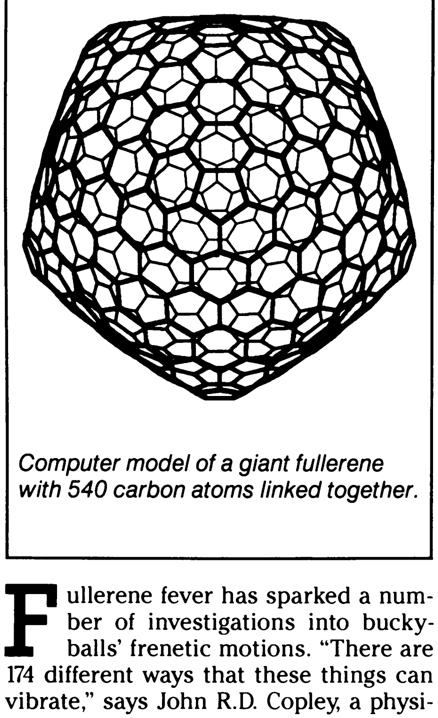
"It could be the world's smallest helium balloon," says Smalley, who envisions several applications for fullerene cages.

"The future is almost certainly putting something in it. And there's enough space inside for almost anything," says Weaver. Ross' approach of jamming an energized atom into a fullerene yields too few successes to be a useful way to produce these complexes. But Whetten thinks chemists will develop a multistep chemical operation to cut open a few carbon bonds, put the passenger molecule inside, then reseal it again. Or, he says, someone might find a way to incorporate a foreign molecule as the fullerene forms in soot.

In theory, atoms would lie suspended within the carbon sphere, where they could tumble freely, says Jerzy Cioslowski, a chemist at Florida State University in Tallahassee. Using a supercomputer, Cioslowski has analyzed the energies involved in putting hydrogen, nitrogen or a carbon monoxide molecule inside a buckyball. He has also investigated other compounds. It appears that a buckyball would trap the molecule but would not react chemically with it, he says.

Thus, the buckyball "may well signal the arrival of a new kind of chemistry: the endohedral chemistry," Cioslowski asserts in the May 22 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY. "By manipulating the size and the composition of the cages, one may expect to be capable of altering the properties of the trapped molecules. This may allow one to design clusters that would act as molecular-scale reaction tanks."

At Wuppertal University in Germany, Dirk Bakowies and Walter Thiel modeled possible structures for even larger fullerenes. Some would contain seven-member carbon rings in addition to the six- and five-member rings that characterize buckyballs. In the May 8 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, they describe optimal structures for fullerenes with up to 540 carbon atoms. These bigger fullerenes tend to have flat areas, they report.



Bakowies and Thiel/Journ. Am. Chem. Soc., May 1991

Computer model of a giant fullerene with 540 carbon atoms linked together.

Fullerene fever has sparked a number of investigations into buckyballs' frenetic motions. "There are 174 different ways that these things can vibrate," says John R.D. Copley, a physicist at the National Institute of Standards and Technology in Gaithersburg, Md. For example, each buckyball could flatten a little and bulge at the side and then return to its round shape. Or the balls could expand and contract as if breathing. Or the pentagon facets might push out as the hexagonal ones contract. "What you'd like to know is what the vibrational modes are and what kinds of energies are associated with these vibrational modes," says James D. Jorgensen of Argonne (Ill.) National Laboratory.

Then, too, the balls can spin — freely and continuously, or sporadically in a ratchet-like fashion. Often, they move quite fast at high temperatures, says Copley, who shoots neutrons at buckyballs to study the molecules' motions. "It's a random set of impulses, keeping these things sort of tumbling around every which way," he says. Working with University of Pennsylvania investigators, his group found that about 30 percent of the buckyball solid is orientationally disordered at 14 kelvins. Some still move, but others sit still, facing every which way.

This description fits well with findings from IBM's Almaden Research Center in San Jose, Calif. At about 250 kelvins, buckyballs undergo an abrupt change: "The balls spin very readily, almost as if the were in the gas phase," says IBM physicist Donald S. Bethune. When cooled below that temperature, they tend to stop — but every so often they flip very quickly partway around. Using nuclear magnetic resonance, Bethune found that the balls need three times as much energy to twist and take much longer to rotate at these cooler temperatures.

Li and his co-workers describe other temperature-related changes in the July 26 SCIENCE. The researchers used the tip of a scanning tunneling microscope to image the growth of thin films of buckyballs on a gallium arsenide substrate at temperatures ranging from 300 to 470 kelvins. At the lower limit, the C_{60} layers showed defects and irregularities. They failed to deposit uniformly, and islands with buckyballs three molecules deep emerged. The gallium arsenide atoms seemed to affect the buckyballs by causing ridged regions to develop in the film.

At 470 kelvins, however, the material seemed almost perfectly ordered. A few ridges remained at the edges of the sample, but a broad, flat region formed in the center, where buckyballs lined up with no regard to the underlying substrate, Li says.

Thicker films of buckyballs take on a looser structure, according to a report in the July 12 SCIENCE. Eric J. Snyder of UCLA and Mark S. Anderson of the Jet Propulsion Laboratory in Pasadena, Calif., showed that thick C_{60} films, when deposited on a calcium fluoride surface, arrange with the carbon molecules at the corners of cubes and with one extra carbon in the cube's faces. The researchers used atomic force microscopy to scan the film surface, then measured the distance between humps, which corresponded to molecules. Anderson and Snyder compared this distance with that of different structural configurations to decipher the arrangement of atoms. They suggest that this more open lattice provides more room in which the buckyballs can freely rotate.

Ordered or disordered, spinning or twisting, superconducting or lubricating, the superstar spheres display "a lot of things that point to a lot of unusual properties," says Ross. Already, "there's a lot of predicted applications," he adds. "But I bet something will come out of this that people hadn't thought about." ☐