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Bubbles hotter than the Sun

29 April 1995 by **Lawrence A. Crum** and **Kenneth S. Suslick**
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TAKE a jar of water, pass sound waves through it and, hey presto, it gives off light. How can this be? For one thing, visible light has so much more energy than sound waves that to turn sound into light you would have to boost the sound's energy a trillionfold, roughly equivalent to focusing all the sunlight striking the Earth onto about 100 square metres.

It turns out that when sound waves are passed through water, they generate tiny bubbles that are expert at focusing energy. And in the process, these bubbles can reach temperatures that are hotter than the surface of the Sun and pressures tens of thousands of times that of the Earth's atmosphere, opening the way to exotic chemical reactions using astonishingly simple equipment (see "Sounding out chemistry"). And researchers now suspect that they may get hotter still - perhaps even hot enough to achieve the elusive nuclear fusion.

Sonoluminescence, the process of turning sound into light, was discovered over 60 years ago, but it was not until 1959 that Erwin Meyer and Heinrich Kuttruff from the University of Göttingen in Germany, discovered that the light came from the collapse of tiny bubbles produced by the sound field, a process called acoustic cavitation (see Diagram).

Concentrated energy

Bubbles can unleash extraordinary amounts of energy when they collapse; for example, if water passes over an obstruction such as a ship's propeller or a turbine blade, bubbles can be generated which, when they collapse, can punch a hole in solid brass or steel. But the concentration of energy needed to turn sound into light is even higher than this.

Sound waves are simply pressure waves alternately compressing and expanding the medium through which they move. Imagine what happens if they pass through liquid. When the pressure drops the liquid effectively boils, forming a bubble that begins to expand, and when the pressure rises again the bubble is forced to collapse. At this stage, the gas inside it is greatly compressed and heated to a very high temperature, and light is emitted.

In 1986, Ken Suslick at the University of Illinois used chemical rate equations to infer that collapsing bubbles in a sound field could reach temperatures of around 5000 K. In 1993, using sophisticated computer models of bubble collapse, Andrea Prosperetti of Johns Hopkins University in Baltimore calculated even higher temperatures of around 7000 K, approximately the temperature of the surface of the Sun, and higher than the temperature of an acetylene torch used to cut hardened steel. Chemists were thrilled at the prospect of such high temperatures from such simple equipment - a jar

of liquid and a sound field. Even though the overall temperature of the liquid stays about the same, there are many thousands of tiny gas bubbles that reach temperatures of thousands of degrees, which makes it possible to break apart molecules and produce chemical reactions that would otherwise be very hard in an ordinary laboratory.

Meanwhile, physicists have been trying to understand exactly how sonoluminescence works. One clue comes from the way the light emissions are distributed, sometimes evenly throughout the water, and sometimes concentrated as intense bands of light at certain points. It turns out that these intense bands coincide with the regions where sound is most intense, in the acoustic "standing waves". These are combinations of forward and reverse waves that look like a single stationary wave, and that occur when a wave moving in one direction is reflected back from a boundary.

But whether it is concentrated in the bands or not, the light comes from so many different parts of the liquid that it must involve the collapse of many different bubbles. And any attempt to understand what is really going on in more detail runs up against the problem that this multiple bubble sonoluminescence is just too messy - imagine trying to understand what is happening in a thousand different bubbles, emitting light at different places.

Fortunately, in 1990 Felipe Gaitan, a graduate student at the University of Mississippi managed to come up with a way out of the messiness when he devised a simple system containing a single "levitated" sonoluminescing bubble. If there is an acoustic standing wave in the middle of the liquid, the forces associated with this standing wave try to move the bubble towards the strongest part of the sound field - that is, towards the middle of the container.

But the bubble is also trying to rise to the surface of the liquid because of its inherent buoyancy. Gaitan tweaked the sound field until the two forces exactly balanced, and levitated the bubble at a fixed position in the liquid. By reducing the amount of gas that was dissolved in the liquid, he could force a single bubble to grow and collapses reaching a bigger size during each successive cycle. Eventually, he found just the right conditions and the bubble glowed like a tiny star.

The discovery of single bubble sonoluminescence (SBSL) made it possible to study sonoluminescence in much more detail than before. By scattering light from a laser beam off the bubble, we watched the violent oscillations, and discovered that, true to our expectations, the light flash was emitted when the bubble imploded. More surprisingly, though, the bubble didn't destroy itself when it collapsed, but reappeared out of the ashes of the implosion.

There were other surprises in store. According to Prosperetti's calculations, the light flash should last about 20 billionths of a second. But in 1991, Seth Putterman and his colleagues at the University of California, Los Angeles, had shown that Prosperetti's predictions were out by a factor of a thousand. They discovered that the light flash lasted for less than 50 trillionths of a second, and the spectrum of the emitted light seemed to show that the temperature inside the bubble was not thousands of degrees, as suggested by Prosperetti, but tens of thousands.

In his calculations, Prosperetti had assumed that when the bubbles collapse, the gas inside is compressed by thousands of times its normal pressure, heating it dramatically. This, he believed, would cause the gas to give off light to shed its newly acquired energy. His calculations and our light-scattering experiments showed that the bubble takes about 20 billionths of a second to collapse, so he assumed that the gas would be heated for the same length of time. But if the hot gas is responsible for the light flash, why should the flash be so much shorter than the time the gas is heated? And why should the temperature be so much hotter than predicted?

One possible explanation is that the inside of the bubble is not heated all at once. Back in 1960, Peter Jarman, an Australian physicist, suggested that a shock wave developed inside the sonoluminescing bubble and that this was responsible for heating the gas. At the time there was no evidence to support this, and Jarman's views were largely ignored. But in the light of Putterman's 1991 experiments and some more recent research by Mike Moran and Willie Moss of the Lawrence Livermore Laboratory in California many physicists began to wonder whether Jarman was right after all.

Two years ago, Cheng Chin Wu and Paul Roberts of UCLA tried to work out what would happen to the gas if a shock wave were created. They assumed that things behave more or less according to Prosperetti's theory until the final stage of collapse. By then, the outside of the bubble could be moving towards the centre faster than the speed of sound, which would launch a shock wave into the centre of the bubble, in much the same way that Concorde's supersonic speeds generate sonic booms. As the molecules in the shock wave all try to arrive at the centre of the bubble at once, they bounce against one another causing the shock wave to rebound. During the implosion, the gas at the centre is heated, but when the shock wave rebounds it allows the gas to expand and cool very rapidly.

Wu and Roberts decided that the gas would therefore be heated for only a very short time, in line with the experimental measurements of the flash duration. They also realised that the energy generated when the bubble collapsed would be distributed over a much smaller volume than had been assumed previously - only the molecules in the very centre would be affected. This would give a higher concentration of energy, and therefore higher temperatures. Wu and Roberts decided that shock waves were the answer, explaining both the rapid flash and the high temperatures seen in experiments.

Noble mystery

Investigations of SBSL have also raised plenty of new questions. For example, in October last year Robert Hiller, from Putterman's group at UCLA, reported in Science that the presence of noble gases such as argon, helium or xenon seemed to be crucial for the sonoluminescence. They discovered this almost by accident. When they filled their luminescing bubble with air they saw plenty of light, but when they filled it with nitrogen or oxygen - the two main constituents of air - there was hardly any light. They realised that air contains a small but significant impurity of argon and so they tried adding a small amount of argon to the nitrogen. To their surprise, they discovered that a mixture containing just 0.1 per cent argon boosted the luminosity by a factor of nearly 30. Helium or xenon worked just as well. For now, no one knows why a small amount of a noble gas should produce such a dramatic change.

Meanwhile, the extreme conditions created during sonoluminescence have raised the exciting, albeit highly controversial idea that SBSL could be used to create nuclear fusion. Nuclear fusion is the energy source that drives the Sun and other stars. Deep inside the Sun, where the gravitational force is enormous, the nuclei of deuterium, a heavy isotope of hydrogen, are forced to fuse to form helium nuclei, releasing tremendous amounts of energy in the process. For many years, physicists have been trying to produce controlled fusion on Earth, because hydrogen is so plentiful here that this could provide a virtually unlimited energy source. But although billions of dollars have been spent on fusion research, we are still at least twenty or thirty years from a commercial process.

The main problem is that before fusion can take place the temperatures and pressures must be extremely high, conditions that are very difficult to reach and control. Could they be reached in sonoluminescence? Using the shock-wave model, Wu and Roberts calculated that temperatures in SBSL could be as high as 100 million degrees. But this was for a highly idealised situation and not

expected to be borne out in the laboratory, since Wu and Roberts had to make assumptions about the way gases behave at high temperatures and pressures.

But last November, at a meeting of the Acoustical Society of America in Houston, Moss reported more realistic calculations. He used sophisticated computer codes that use equations to represent the behaviour of gases under extreme conditions. To everyone's surprise, he reported that the temperatures in the imploded shock wave could still reach 2 million degrees - roughly half of what would be needed for fusion. What was more, the pressures would be so enormous - probably millions of atmospheres - that the density of the gas could reach that typical of metals.

Moss pointed out that while these astonishing temperatures and pressures are not high enough for nuclear fusion, it might be possible to increase the temperatures and pressures further. One way would be to apply an impulsive force or boost to the bubble just before the shock wave is launched into the gas, and thereby obtain much greater compression.

Achieving fusion from sonoluminescence seems rather remote, but there are various other approaches that might just work. For example, the system that is currently used to produce SBSL runs at a frequency of tens of thousands of cycles per second, so the bubble giving out the light has very little time to grow before it is forced to collapse. A lower frequency should create bigger bubbles and perhaps more compression.

Large bubbles may be too distorted by gravity to collapse in a spherically symmetrical way, and because this means the energy of the collapse will not all be focused in the centre, it would limit the ultimate temperature reached. But if an SBSL system were to be built in a gravity-free environment, such as a space station, it might be possible to overcome some of the limitations imposed by gravity on Earth, and use space to help us achieve temperatures and pressures high enough for fusion.

Even if none of these possibilities finally comes off, it seems likely that the extraordinary conditions generated during sonoluminescence will open up many exciting new avenues in years to come.

Sounding out chemistry

NEARLY seventy years ago, Princeton scientist Alfred Loomis first noticed the chemical effects of ultrasound - sound waves whose frequency is too high to be audible to humans. But the field of sonochemistry lay fallow until the 1980s when inexpensive and reliable laboratory generators of high-intensity ultrasound became available.

Sonochemistry occurs because of acoustic cavitation - the formation, growth, and implosive collapse of bubbles in a liquid irradiated with high-intensity sound or ultrasound. The collapse generates intense local heating and extreme pressures, but for very short timespans, typically less than a millionth of a second.

Because the bubbles are tiny, the hot regions that they generate then cool very rapidly, at rates of more than 10^{10} degrees per second - a million times faster than cooling a red-hot metal poker by plunging it into ice water. The immense local temperatures and pressures and the extraordinary heating and cooling rates generated by the collapsing bubble mean that ultrasound is an extremely unusual and potentially very useful method of generating high-energy chemistry.
One of many exciting applications of sonochemistry lies with amorphous metals. If a molten metal alloy can be cooled quickly enough, it can freeze into a solid before it has a chance to crystallise properly. Unlike normal metals or alloys, the resulting amorphous alloys have no crystalline structure

on a scale of more than a few hundred atoms. They thus can have unique electronic and magnetic properties, and can also resist corrosion, but are hard to make because the cooling has to be very rapid.

In 1992, three researchers in my group at the University of Illinois managed to capitalise on the rapid cooling rates that sonochemistry offers. Seok-Burm Choe, Andrzej Cichowlas and Mark Grinstaff used ultrasound to decompose solutions of organometallic compounds and create hot clusters of metal atoms, which amalgamated and cooled very rapidly to form amorphous metal powders made up of nanometre-sized metal clusters.

This means that it may be possible to make unusual materials at low overall temperatures. For example, we used iron pentacarbonyl to produce amorphous iron, which has a very high surface area and is an active catalyst for several important reactions, for example converting carbon monoxide from coal into liquid fuel. And magnetic measurements reveal that the amorphous iron is a very soft ferromagnet - in other words, it quickly forgets its original magnetisation and adopts a new one when a magnetic field is applied. Such materials are excellent for electrical transformer cores or magnetic recording heads.

At the other end of the scale, sonochemistry's extreme temperatures could also benefit industries or governments struggling to clean up water sources contaminated by small amounts of halocarbons, pesticides, or other toxic or carcinogenic compounds. Everyone knew that applying ultrasound to aqueous solutions yielded hydrogen and hydrogen peroxide, but Peter Riesz at the US National Institutes of Health recently proved that aqueous sonochemistry also yields the hydroxyl radical, which is an extremely potent oxidising agent normally formed in flames. In other words, the high temperatures of cavitation create flame-like conditions inside the liquid water, breaking the water's hydrogen-oxygen bond and forming the hydroxyl - normally a very difficult feat.

Other researchers have also been hard at work in similar areas. Over at the Hahn-Meitner Institute in Berlin, Arnim Henglein's team has turned up many other similarities between sonochemistry and combustion chemistry, and Michael Hoffmann at the California Institute of Technology is exploring applications for these extremely high-energy chemical reactions for cleaning up contaminated water supplies.

High-intensity ultrasound can be used to increase the speed of reactions at metal surfaces substantially, and this has become an important synthetic technique for many chemical reactions, especially those involving reactive metals such as magnesium, lithium or zinc, which are particularly important for synthesising pharmaceuticals and rare chemicals. This approach was first advocated by Pierre Renaud in France in the 1950s, and has been developed more recently by Jean-Louis Luche at the University of Toulouse.

Chemists are also excited by the shock waves generated when the bubbles collapse. These are like tiny depth charges in the liquid. If they occur in the presence of metal powder, they can smash nearby powder particles together at such high speeds that the particles actually melt at the points where they collide. This was discovered in 1990 by Stephen J. Doktycz and Dominick Casadonte in my group at the University of Illinois. Such collisions can produce striking changes in surface texture, composition, and reactivity of the powders.

Recently, Gareth Price at the University of Bath has been studying how to use sonochemistry to break up polymers dissolved in organic solvents. The polymer chains are split mechanically by shock waves when the solvent is irradiated with ultrasound. Price has used this to synthesise block copolymers, long-chain polymers with two or more different, but linked, parts - like a train made up of passenger

cars in front and freight cars at the back. The idea is that block copolymers can combine the useful properties of their constituent parts.

Ultrasound is also useful for synthesising biomaterials, particularly micrometre-sized spheres with shells made from protein molecules that are bonded together sonochemically. Such microspheres are smaller than red blood cells and can be used to carry drugs and medical imaging agents through the bloodstream. One recent example is the use of high-intensity ultrasound by Mike Wong, a student at Illinois, to make long-lived haemoglobin microspheres suspended in water, which could act as a blood substitute to carry oxygen from the lungs to the rest of the body (Technology, 17 December 1994).

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