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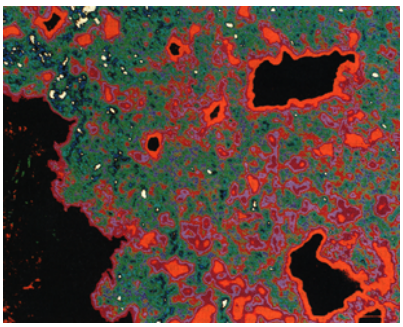
LIGHT COMES FROM ULTRASONIC CAVITATION IN PICOSECOND PULSES

Many applications of ultrasound, such as welding plastics or sterilization of medical equipment, exploit cavitation, the rapid expansion and collapse of bubbles as sound waves pulse through a liquid. This phenomenon that has proved to be so utilitarian is also the source of great fascination and mystery: During cavitation the collapsing bubbles develop extremely high temperatures and pressures and emit visible radiation. Recent experiments have elucidated just how extreme the properties of cavitation bubbles are and have also suggested what potential new applications the bubbles might have. In one paper, Bradley Barber and Seth Putterman of the University of California at Los Angeles report that the light emitted during cavitation-known as sonoluminescence-emerges in flashes that are less than 50 picoseconds long, far shorter than anyone had expected, and that the pulses repeat with clocklike precision.' In other work, Edward Flint and Kenneth Suslick of the University of Illinois at Urbana-Champaign have confirmed,2 by the most direct measurements to date, the long-standing expectation[3] that the temperature during cavitation soars above 5000 K. A number of researchers have been exploiting these high temperatures for several years by using acoustic waves to accelerate various chemical reactions. Suslick and his colleagues recently reported a new application along these lines-the formation of amorphous iron.4



Amorphous Fe powder, seen in a false color TEM, at the University of Illinois. The powder is produced when the organometallic compound iron pentacarbonyl is irradiated with ultrasound. The extreme conditions within the cavitating bubbles help form the powder: The high heat during compression dissociates the compound, and the rapid expansion cools the iron before it has a chance to crystallize.

Sonoluminescence

It has been known since 1934 that a cavitating liquid emits visible light. This conversion of energy from sound to light was first interpreted as blackbody radiation from the hot, compressed bubbles, but it is now known that the radiation can exhibit a discrete spectrum due to excited atoms and molecules, superposed on a broad background. As Putterman likes to point out, somehow the diffuse energy densities of about 10^{-11} eV/atom in a sound field are being concentrated into the energies of a few electron volts per atom that are needed to produce visible radiation. Exactly how this energy concentration occurs has never been explained, but it certainly involves complex processes. In the compressed state the temperatures and pressures are so high and change so rapidly that it is not clear whether equilibrium thermodynamics applies.

Putterman and Barber measured the width of the flashes of sonoluminescence on a single, stable bubble. The technique for stabilization was developed by Lawrence Crum (University of Mississippi) and Felipe Gaitan (now at the Naval Postgraduate School)." The key is to excite a large-amplitude standing wave, trapping just one bubble at a large antinode. To this end the water must be degassed so that the appearance of transient cavitation is suppressed. One common configuration is a radial mode in a spherical flask, where the bubble is levitated by acoustical forces at the center. One of the big surprises in the measurements that Crum and Gaitan made was that the bubble emitted one flash of light for each cycle of the sound field. The researchers had expected that the light would come in a burst as the bubble collapsed and broke up, followed by a hiatus of several cycles while a new bubble grew to the critical size necessary for sonoluminescence. But apparently the single bubble was very stable.

Using a spherical single-bubble system, Barber and Putterman have found that the light, which is visible

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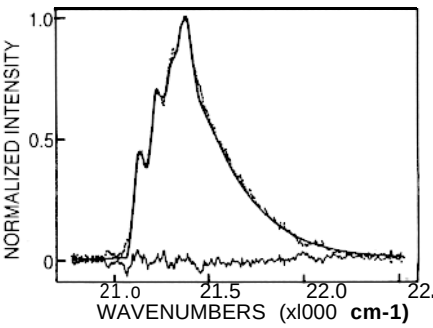

Emission spectrum **for C2 during sonoluminescence (data points) is fit with a theoretical curve (thick black line) to determine the temperature during cavitation. Thin black line along horizontal axis is the difference spectrum. From these data University of Illinois researchers2 found that the bubbles formed in cavitation are heated to 5050 K.**

to the unaided eye, comes in pulses that are shorter than 50 psec and contain a few hundred thousand photons. The pulses are so short that even the fastest photomultiplier tube the researchers could find (with a rise time of 170 psec) could not fully resolve them. The light pulses are also emitted with an impressive regularity, with the period of the acoustic wave. Together with Robert Hiller, Katsushi Arisaka and Harold Fetterman, Barber and Putterman made measurements using a time interval meter that indicate that the jitter in the time between flashes is less than 50 psec. More precise measurements of the flash duration will require the higher resolution of a streak camera. Such measurements are being planned by the UCLA group, in coop eration with the Hamamatsu Corpo-' ration, and by Gaitan, Anthony Atchley and Xavier Maruyama of the Naval Postgraduate School, who are collaborating with Michael Moran and Mark Lowry of Lawrence Livermore Lab. The latter group will use a camera at Livermore, whose resolution is about 25 psec.

The narrow pulse width suggests some cooperative phenomena such as laser action, superradiance or superfluorescence. Putterman and Barber have estimated that during the bubble's compressive cycle the distance between emitting sources is much less than the wavelength of light, and so some correlation in the outgoing photon field might be expected. The UCLA researchers plan to determine whether the sonoluminescence is coherent. Once the phenomenon is better understood, one will be able to assess whether applications lie ahead. But at the very least, it may be a potentially useful source of picosecond pulses of light.

Sonochemistry

By contrast with the stable-cavitation experiments, Suslick and his team at the University of Illinois study systems in transient cavitation. In his system, a large-amplitude acoustic horn drives many cavitation events in the liquid of interest. Suslick and Flint recently exploited sonoluminescence to estimate the temperature of cavitation. They used ultrasound to produce rotational and vibrational excited states of diatomic carbon molecules from silicon oil, and they measured the spectra emitted by these C2 molecules. The measured spectra were fit by a theoretical expression in which the rotational and vibrational temperatures were adjustable parameters. The Illinois researchers found that these two temperatures were equal, as one would expect for a system in thermal equilibrium. The temperatures found from fits to two different bands agreed well, and the average value was 5050 $\pm$ 150 K. (See the figure on this page.) Even if one were to quibble with the assumption that the system was in equilibrium, this temperature would at least be a lower limit on the average energy of excitation. The Illinois team had made earlier estimates of the temperature based on comparative reaction rates, with similar results.

The high temperatures of cavitation have already spawned the field of sonochemistry, in which the intense heat, as well as the high pressures (above 500 atmospheres), of the cavitation bubbles greatly enhances reactivities. Ultrasound can, for example, decompose organic compounds, "crack" crude oil, emulsify liquids, remove nonreactive coatings from surfaces or accelerate the reactions of active metals.

Recently Suslick and his colleagues Seok-Burm Choe, Andrzej A. Cichowlas and Mark W. Grinstaff exploited the very rapid heating and cooling of ultrasonic cavitation to synthesize amorphous iron. They acoustically irradiate a solution of iron pentacarbonyl, Fe(CO)5. During the compression stage the high temperatures and pressures free the iron atoms from the CO molecules, and during the expansion the iron cools. But the quench rate is so rapid that the iron does not have a chance to crystallize as it cools, and instead forms an amorphous powder. The Illinois researchers estimate the cooling rate to be well above the rates of 10^5–10^7 K/sec that are required to produce most metallic glasses. The resulting powder is quite pure, containing less than 3% carbon and 1% oxygen by weight. Industrial processes typically produce metallic glasses containing over 20% of other alloying elements, which are required essentially to impede the crystallization during cooling.

The Illinois experimenters performed a large number of tests to strengthen their conclusion that the powder formed was truly amorphous. The tests they ran included scanning and transmission electron microscopy, differential scanning calorimetry, x-ray powder diffraction and electron-beam microdiffraction. (A picture of the iron powder made with a transmission electron microscope is shown on page 17.) In several of these measurements there was no sign of a crystalline form until the sample was heated above 350 °C, a temperature at which crystallization can occur.

The surface area of the iron powder is quite large, making it an effective catalyst. The Illinois team used the powder to catalyze hydrogenation of CO by the Fisher-Tropsch process. But the metallic properties of the amorphous iron are of even greater potential commercial interest for such things as magnetic tapes. Together with Myron Salamon of Illinois's physics department, Suslick and his fellow chemists have determined that the iron powder is a very soft ferromagnet; that is, it shows little of the hysteresis that could hinder its performance in a recording head. But is the acoustic production of these iron powders commercially viable? Right now, Suslick told us, his group can produce powder at the rate of grams per hour with, very roughly, 100 W input energy. Suslick claims that scale-up is possible because there are commercially available high-intensity ultrasonic flow systems. The University of Illinois apparently sees promise in the process: Together with Research Corporation Technologies, the university has filed for a patent on it.

-BARBARA GOSS LEVI

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