

# The mechanochemical effects of ultrasound

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**Abstract:** The chemical effects of ultrasound are the result of acoustic cavitation: the formation, expansion, and implosive collapse of bubbles in liquids irradiated with ultrasound. The compression of such bubbles generates intense local heating, with transient temperatures  $\gg 5000$  K and pressures of roughly 1000 atmospheres, but with sub-microsecond lifetimes. There are diverse mechanochemical aspects of such sonochemistry, particularly with liquid-solid mixed phase systems. Ultrasonic irradiation of liquid-solid slurries produces a remarkable effect: extremely high speed inter-particle collisions. Turbulent flow and shockwaves produced by acoustic cavitation can drive metal particles together at sufficiently high velocities to induce effective melting upon collision. A series of transition metal powders have been used to probe the maximum temperatures and speeds reached during such interparticle collisions. Metal particles that are irradiated in hydrocarbon liquids with ultrasound undergo collisions at roughly half the speed of sound and generate localized effective temperatures of  $\gg 3000$  K at the point of impact for particles with an average diameter of 10 nm. Through such processes, liquid-solid sonochemistry can drive a variety of unusual reactions that normally occur only under extreme conditions. Examples include carbonylation of early transition metals, intercalation into layered inorganic solids, synthesis of amorphous metal powders, and the dramatic activation of some heterogeneous catalysts.

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The chemical effects of mechanical actions were reported as early as the 1890's, when Carey-Lea discovered an apparently non-thermal chemistry associated with the grinding of metal chlorides, the formation of free metal and  $\text{Cl}_2$ . At the turn of the century, the definition by Ostwald of "mechanochemistry" set the foundation for its systematic study. The field of mechanochemistry (built by Thiessen, Heinicke, Kubo, and Avvakumov, among others<sup>1</sup>) has revealed an enormous diversity of chemical reactions that occur during solid surface interactions. Our own work on the chemical effects of ultrasound in liquids and liquid-solid systems has addressed similar phenomena induced by various mechanical processes that ultrasound can create, including acoustic cavitation, turbulent flow, microjet formation, and shock waves.

The chemical effects of ultrasound are diverse and include substantial improvements in both stoichiometric and catalytic reactions.<sup>2-5</sup> In some

cases, ultrasonic irradiation can increase reactivities by nearly a million-fold.<sup>6</sup> The chemical effects of ultrasound fall into three areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis (which overlaps the first two). Because cavitation cannot occur, chemical reactions are not generally seen in the ultrasonic irradiation of solids or solid-gas systems.

## Mechanical origins of the chemical effects of ultrasound

The ultrasonic irradiation of liquids produces high energy chemical reactions.<sup>7</sup> Such sonochemistry, however, does not come from a direct interaction with molecular species. The frequencies and wavelengths of ultrasound (roughly 15 kHz to 1 GHz and 10 to  $10^4$  cm) are not of molecular dimen-

## INTERPARTICLE COLLISIONS

Sn (m.p. 232°) and Fe (m.p. 1535°)

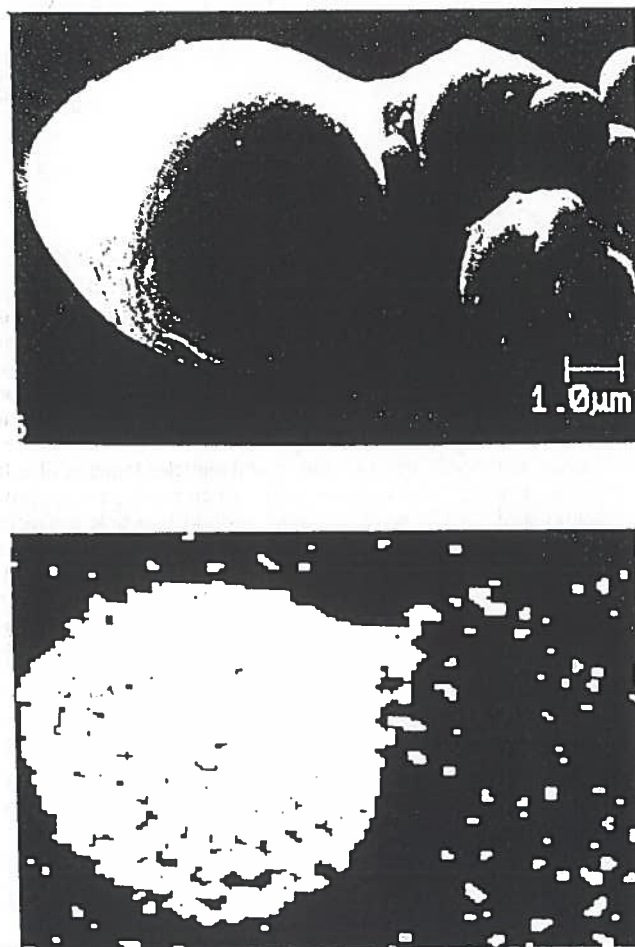


Fig. 1 Scanning electron micrograph and Auger elemental map of Sn and Fe interparticle collisions driven by ultrasonic irradiation of mixed slurries in decane under Ar at 20 kHz and 50 W/cm<sup>2</sup>. Note the neck formation at the point of collision between the larger Sn particle on the left and an iron particle on the right. In the Auger elemental map, Sn is shown in white.

sions. Sonochemistry derives principally from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. Compression of a gas generates heat. When the compression of cavities occurs in liquids irradiated with ultrasound, the collapse is more rapid than thermal transport. Thus one generates a short-lived, localized hot-spot in an otherwise cold liquid. Bubble collapse induced by cavitation produces intense local heating, high pressures, and very short lifetimes. These hot spots have temperatures of roughly 5000°C, pressures of about 1000 atmospheres, and heating and cooling rates above 10<sup>9</sup> K/s.<sup>7-9</sup> Thus, cavitation serves as a means of concentrating the diffuse energy of sound. It is generally accepted that this hot-spot is the source of homogeneous sonochemistry; al-

ternative mechanisms involving electrical microdischarge have been occasionally proposed, most recently by Margulis, but are generally out of favour and do not appear consistent with observed data.

Determination of the temperatures reached in a cavitating bubble was a difficult experimental problem. The transient nature of the cavitation event precludes direct measurement of the conditions generated during bubble collapse. Chemical reactions themselves, however, can be used to probe reaction conditions. The effective temperature realized by the collapse of a cavitation bubble can be determined by the use of competing unimolecular reactions whose rate dependencies on temperature have already been measured. This technique of "comparative-rate chemical

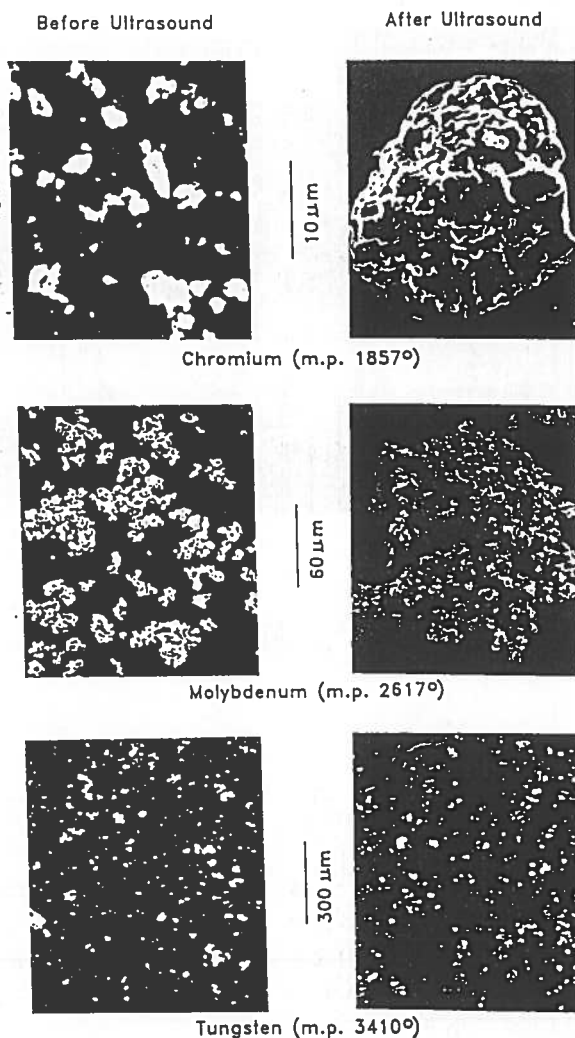


Fig. 2 Scanning electron micrograph of Cr, Mo, and W powder after ultrasonic irradiation of decane slurries under Ar. The melting points of these metals are 1857°, 2617°, and 3410°C, respectively.

thermometry" was used to determine the effective temperature reached during cavity collapse<sup>8</sup>. The effective temperature of these hot spots was measured at  $5200 \pm 650$  K in the gas-phase reaction zone and  $\approx 1900$  K in the initially liquid zone surrounding the collapsing bubble. Of course, the comparative rate data represent only a composite temperature: during the collapse, the temperature has a highly dynamic profile, as well as a spatial temperature gradient in the liquid surrounding the gas phase hot spot. Sonoluminescence studies have provided an alternative, spectroscopic probe of the cavitation event. The observed emission from hydrocarbons comes from excited state  $C_2$  (Swan band transitions,  $d^3\pi_g - a^3\pi_u$ ) which have been modelled with synthetic spectra as a function of rotational and vibrational temperatures. From comparison of synthetic to observed spec-

tra,<sup>9</sup> the effective cavitation temperature of excited state  $C_2$  is  $5050 \pm 150$  K.

Ultrasonic cavitation in liquid–solid systems produces related mechanical phenomena. Cavitation near extended liquid–solid interfaces is very different from cavitation in pure liquids.<sup>10</sup> Whenever a cavitation bubble is produced near a boundary, the asymmetry of the liquid particle motion during cavity collapse often induces a deformation in the cavity. The potential energy of the expanded bubble is converted into kinetic energy of a liquid jet that extends through the bubble's interior and penetrates the opposite bubble wall. Because most of the available energy is transferred to the accelerating jet, rather than the bubble wall itself, this jet can reach velocities of hundreds of meters per second. Because of the induced asymmetry, the jet often impacts the local

## THE EFFECT OF ULTRASONIC IRRADIATION ON PARTICLE MORPHOLOGY: $TaS_2$

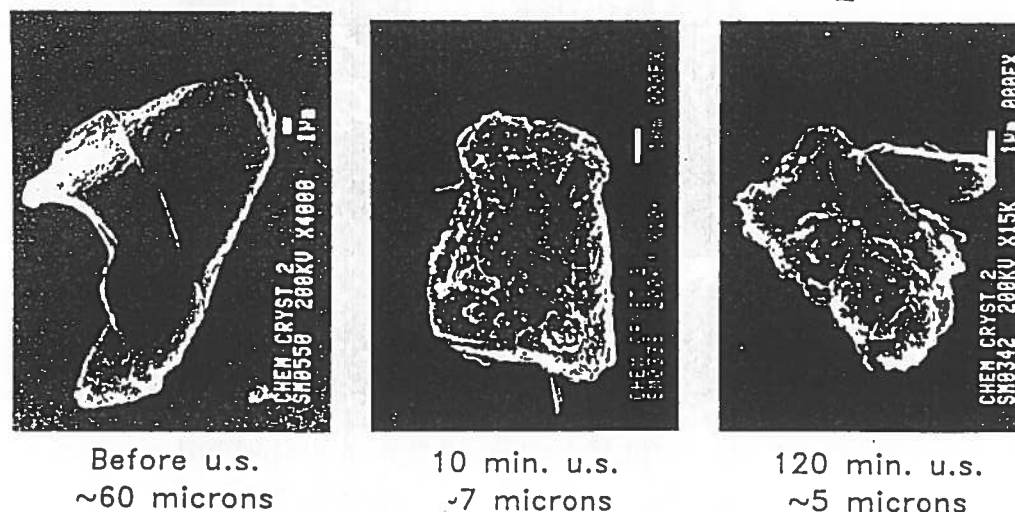


Fig. 3 Scanning electron micrographs of  $TaS_2$  powder before, after 10 minutes, and after 120 minutes of ultrasonic irradiation of slurries in decane under Ar at 20 kHz and  $\approx 50$  W/cm<sup>2</sup>. Note changes of magnification.

boundary and can deposit enormous energy densities at the site of impact. The impingement of microjets and shockwaves on the surface creates the localized erosion responsible for ultrasonic cleaning and many of the sonochemical effects on heterogeneous reactions. The erosion of metals by cavitation generates newly exposed, highly heated surfaces and ejects metal from the surface. The importance of this process to corrosion and erosion phenomena of metals and machinery has been thoroughly reviewed elsewhere.

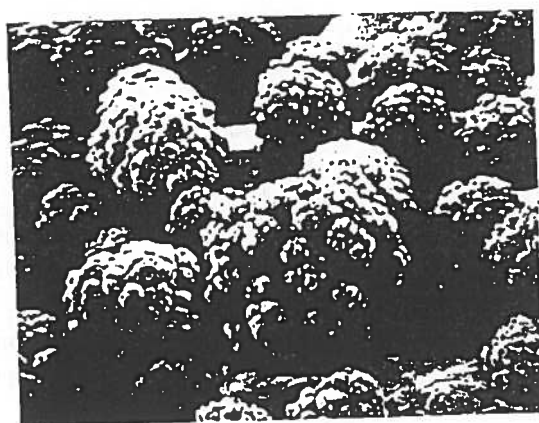
Distortions of bubble collapse depend on a surface several times larger than the resonance bubble size. Thus, for ultrasonic frequencies of  $\approx 20$  kHz, damage associated with jet formation cannot occur for solid particles smaller than  $\approx 200$   $\mu$ m. In these cases, however, the shockwaves created by homogeneous cavitation can create high velocity interparticle collisions. The turbulent flow and shockwaves produced by intense ultrasound can drive metal particles together at sufficiently high speeds to induce effective melting at the point of collision (Fig. 1).<sup>11</sup> These interparticle collisions are capable of inducing striking changes in surface morphology, composition, and reactivity. A series of transition metal powders were used to probe the maximum temperatures and speeds reached during interparticle collisions (Fig. 2).<sup>11,12</sup> Using the irradiation of Cr, Mo, and W powders in decane at 20 kHz and 50 W/cm<sup>2</sup>,

one observes agglomeration and what appears to be localized melting for the first two metals, but not the third. On the basis of the melting points of these metals (1857°, 2617°, and 3410°C, respectively), the effective transient temperature reached at the point of impact during interparticle collisions is roughly 3000°C. From the volume of the melted region of impact, the amount of energy generated during collision was determined. From this, a lower estimate of the velocity of impact is roughly one half the speed of sound!

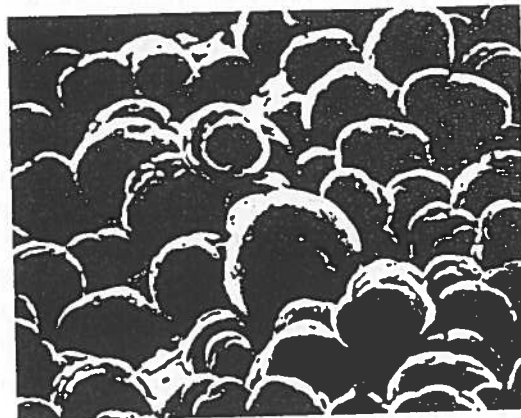
In contrast to the agglomeration of malleable metal powders, fragmentation is observed during ultrasonic irradiation of slurries of brittle solids, such as layered metal sulfides and oxides.<sup>13</sup> Scanning electron microscopy shows both that rapid particle fragmentation occurs (which dramatically increases surface areas) and that substantial surface damage develops as a consequence of the interparticle collisions (Fig. 3). The ability of high intensity ultrasound to rapidly form uniform dispersions of micrometer-sized powders of brittle materials had not been generally recognized.

### Mechanochemical reactions caused by ultrasound

The use of high-intensity ultrasound to enhance



Before U.S.  
~160 microns



60 min. U.S.  
~80 microns

Fig. 4 The effect of ultrasonic irradiation on the surface morphology of Ni powder. High-velocity interparticle collisions caused by ultrasonic irradiation of slurries is responsible for these effects.

the reactivity of metals as stoichiometric reagents has become a routine synthetic technique for many heterogeneous organic and organometallic reactions, especially those involving reactive metals, such as Mg, Li or Zn.<sup>4</sup> The mechanism of the sonochemical rate enhancements in both stoichiometric and catalytic reactions of metals has been revealed with the use of the following protocol: (i) monitor the effect of ultrasonic irradiation on the kinetics of the chemical reactivity of the solids, (ii) determine effects of irradiation on surface morphology and size distributions of powders and solids, and (iii) measure surface composition depth profiles. The power of this three-pronged approach has been proved in studies of the sonochemistry of transition metal powders.<sup>12,14,15</sup> Ultrasonic irradiation of slurries of metal powders leads to dramatic changes in the powder morphology. The high-velocity interparticle collisions produced in such slurries cause smoothing of individual particles (Fig. 4) and agglomeration of particles into extended aggregates (Fig. 2). Surface composition was probed by Auger electron spectroscopy and sputtered neutral mass spectrometry to generate elemental depth profiles of these powders. These studies revealed that ultrasonic irradiation effectively removed the surface oxide coating, which can dramatically improve reaction rates.

Another mechanochemical aspect of ultrasound

in materials chemistry involves the process of molecular intercalation into layered inorganic solids.<sup>13</sup> The adsorption of organic or inorganic compounds as guest molecules between the atomic sheets of layered solid hosts permits the systematic change of optical, electronic, and catalytic properties. Such materials have many technological applications (for example, lithium batteries, hydrodesulfurization catalysts, and solid lubricants). The kinetics of intercalation, however, are generally extremely slow, and syntheses usually require high temperatures and very long reaction times. High-intensity ultrasound dramatically increases the rates of intercalation (by as much as 200-fold) of a wide range of compounds (including amines, metallocenes, and metal sulfur clusters) into various layered inorganic solids (such as  $ZrS_2$ ,  $V_2O_5$ ,  $TaS_2$ ,  $MoS_2$ , and  $MoO_3$ ). Scanning electron microscopy of the layered solids coupled to chemical kinetics studies demonstrated that the origin of the observed rate enhancements comes from particle fragmentation (which dramatically increases surface areas), and to a lesser extent from surface damage. The activation of heterogeneous reagents, especially non-metals, often arises from this effect. The effects of ultrasound on silica, for example, can substantially alter reactivity patterns.<sup>16</sup>

Recently, the use of ultrasound to synthesis amorphous metal powders was reported.<sup>17</sup> This

exciting discovery opens new applications of ultrasound for the low temperature synthesis of unusual phases. Amorphous metallic alloys lack long range crystalline order and have unique electronic, magnetic and corrosion resistant properties. The production of amorphous metals, however, is difficult because extremely rapid cooling of molten metals is necessary to prevent crystallization. Cooling rates of  $\approx 10^6$  K/sec are required; for comparison, plunging red hot steel into water produces cooling at only  $\approx 2500$  K/sec. As discussed earlier, acoustic cavitation can induce extraordinary local heating in otherwise cold liquids and can provide enormous cooling rates, above  $10^9$  K/sec. This provides a new synthetic route to amorphous metal powders using the sonochemical decomposition of volatile organometallics. For example, the sonolysis of iron pentacarbonyl produces nearly pure amorphous iron, which has been thoroughly characterized by a variety of techniques, including X-ray, TEM electron and neutron diffraction, confirming lack of long range order; differential scanning calorimetry, showing crystallization at elevated temperatures; scanning and transmission electron microscopy, characterizing the amorphous solid morphology; and SQUID magnetic susceptibility measurements, revealing that the amorphous iron is a very soft ferromagnet, potentially useful for magnetic shielding or electrical transformer applications.

Catalytic reactions are of enormous importance in both laboratory and industrial applications. Consequently, the use of ultrasound to enhance catalytic reactions has great potential. The effects of ultrasound in this area can occur in three distinct stages: during the formation of supported catalysts, by activation of preformed catalysts, or through enhancement of catalytic behavior during a catalytic reaction. In the cases of modest rate increases, the cause is often simply an increased effective surface area; this is especially important in the case of catalysts supported on brittle solids.

More impressive accelerations, however, have been reported, including hydrogenations and hydrosilations by Ni powder, Raney Ni, and Pd or Pt on carbon. For example, the hydrogenation of alkenes by Ni powder is enormously enhanced ( $>10^5$ -fold) by ultrasonic irradiation.<sup>6</sup> The surface area did not change significantly even after

lengthy irradiation. There is, however, a very interesting effect on the surface morphology. Ultrasonic irradiation smooths, at a macroscopic scale, the initially crystalline surface and causes agglomeration of small particles. Both effects are probably due to interparticle collisions caused by cavitation-induced shockwaves. Auger electron spectroscopy reveals that there is a striking decrease in the thickness of the oxide coat after ultrasonic irradiation, just as in the case of stoichiometric reactions of Cu and Zn. The removal of this passivating layer is probably responsible for the  $>10^5$ -fold increase observed in catalytic activity.

#### Acknowledgments

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