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# Sonochemistry

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## 1. Introduction

Applications of ultrasound in processing and synthesis are widespread and offer unusual and beneficial operating conditions. Two major principles are used in sonochemistry or sonoprocessing: a) mechanical effects for mixing and disintegration and b) high energy processes for radical reactions. Most effects occur in liquids, where sound pressures are able to disrupt the continuum. This generates oscillating bubbles, a process called cavitation. Cavitation is observed in shock tubes, pumps and other hydrodynamic devices. Due to the high frequencies in sonochemistry of between 16 kHz and several megahertz, the dynamics of oscillating bubbles create drastic conditions. Temperatures of several thousand Kelvin, extreme heating or cooling rates of  $10^5$  K/s, and pressures of up to several hundred megapascal are observed in a transient cavities while the bulk conditions in the liquid remain at ambient temperature and pressure. Radiation forces create intense micro and macromixing with high shear forces, which are used in emulsification, homogenization, and fragmentation processes. Asymmetrical bubble oscillations in the vicinity of solid particles lead to liquid microjets and shock waves, which are used in cleaning, dispersion, activation, and fragmentation of solid materials. Besides the main industrial applications in cleaning, emulsification, and welding, other uses of ultrasound, such as solids processing, atomization, crystallization, environmental protection and separation are emerging (Table (1)). Some synthetic methods, for example the Barbier and Grignard reactions, have found industrial

utilization. The growing interest in ultrasound application arises from the development of reliable ultrasound devices in the last years and the need for intensified and environmentally friendly processes with small safe reactor units, better energy yield, and enhanced chemical yield.

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## 2. Fundamentals of Ultrasound

The term ultrasound describes sound waves with a frequency range from 16 kHz up to several megahertz [2]. Vibrational motions are transmitted by oscillating devices into a fluid and cause pressure waves. This varying sound pressure is superimposed on the static pressure of the liquid. Fluids are generally capable to transduce longitudinal waves, whereas solids also can show transversal motion. Above a critical sound pressure, liquids are disrupted by the applied sound pressure and so-called cavities are created. Most sonochemical effects are secondary effects generated by oscillating bubbles.

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### 2.1. Ultrasound in Liquids

Sound waves in liquids are density and pressure waves in which particle oscillations occur in the direction of the wave (longitudinal waves). The displacement around the rest position causes compression and rarefaction disturbances which are transmitted to the connected layers (Fig. (1)). The time-dependent particle displacement  $\xi$  the particle velocity  $v$  and the sound pressure  $p_a$  for plane waves can be described by:

$$\xi = \hat{\xi} \sin(2\pi f t) \quad (1)$$

$$v = \frac{d\xi}{dt} = \hat{v} \cos(2\pi ft) \quad (2)$$

$$p_a = \hat{p}_a \cos(2\pi ft) \quad (3)$$

with the maximum values of particle displacement, particle velocity and sound pressure indicated by circumflexes. In plane waves, the particle velocity  $v$  and the sound pressure  $p_a$  are related by the specific impedance of the liquid

$$\rho_L c_L = \frac{p_a}{v} \quad (4)$$

which is the product of the liquid density  $\rho_L$  and velocity of sound  $c_L$ .

The sound wave transports energy by kinetic energy of the oscillating particles. If we assume an energy density  $E$  given by

$$E = 0.5 \rho_L v^2 \quad (5)$$

which passes through a cross-sectional area  $S$  with the velocity of sound  $c$  we derive the so-called ultrasound intensity  $I$  as the energy flux per unit area:

$$I = 0.5 \rho_L c_L v^2 = 0.5 \frac{\hat{p}_a^2}{\rho_L c_L} \quad (6)$$

The determination of local intensities is quite difficult, and ultrasound devices are mostly characterized by calorimetric measurements. Sound pressure measurements and methods for determining the local intensity with coated thermocouples or by chemical means are still under development [1].

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## 2.2. Cavitation

Sufficiently high sound pressures in liquids create voids or gas- and vapor-filled bubbles. Any liquid has a theoretical tensile strength which characterizes the minimum pressure for disruption. Due to the presence of nuclei such as dissolved gases, solid impurities, and rough walls, cavitation occurs at far lower sound pressures than are theoretically necessary. In nearly any liquid, initial

nuclei are present which show a distinct size distribution and grow under a certain sound pressure. Bubble growth, multiplication, and disappearance in a sound field is still very complex phenomenon.

### 2.2.1. Bubble Behavior in Acoustic Fields

Several types of bubbles are present in cavitating liquids. Empty cavities (true cavitation), gas-filled cavities, vapor-filled cavities or mixtures of gas and vapor can be observed, depending on the applied sound pressure, static pressure, temperature, and the nature of the used liquid. Some of these bubbles disappear because of dissolution of their contents under the sound pressure, some of them oscillate stably over several periods and others collapse violently, followed by the creation of smaller bubbles. The main task in sonochemical applications is the choice of the proper bubble behavior for the desired effect. Bubble motions in a sinusoidal sound pressure field can be described, for example, by the Rayleigh–Plesset equation

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\varrho_L} \left\{ \left( p_\infty + \frac{2\sigma_L}{R_0} - p_v \right) \left( \frac{R_0}{R} \right)^{3\gamma} + p_v - \frac{2\sigma_L}{R} - \frac{4\eta}{R} \right.$$

(7)

which includes the surface tension  $\sigma_L$ , the liquid viscosity  $\eta_L$ , the polytropic exponent  $\gamma$  of the gas inside the bubble, the vapor pressure  $p_v$  and the initial bubble radius  $R_0$  at rest. The solutions of this equation lead to nonlinear bubble wall motions (Fig. (2)). A special case are resonant bubbles, which show damped oscillations. The resonant radius  $R_r$  of such a bubble can be described by Minnaert's formula

$$\varrho_L \omega_r^2 R_r^2 = 3\gamma \left( p_\infty + \frac{2\sigma_L}{R_r} \right) - \frac{2\sigma_L}{R_r} \quad (8)$$

with the circular frequency  $\omega_r = 2\pi f$ .

### 2.2.2. Cavitation Thresholds

A more illustrative description of the bubble motion in an acoustic field can be introduced by the concept of cavitation thresholds for different types of bubble behavior [10]. Depending on the nature of the motion four basic types of cavitating voids are distinguished (Fig. (3)):

- Stable cavitation
- Rectified diffusion
- Dissolving bubbles
- Transient cavitation

In the absence of an acoustic field, a gas bubble in a liquid will slowly dissolve owing to the excess internal pressure required to withstand the surface tension pressure  $2\sigma_L/R_0$ . By applying a changing pressure, the dissolution time can be increased. Very small bubbles will still dissolve, but some bubbles larger than a certain threshold radius can be stabilized in the sound field. These stable oscillating bubbles survive several acoustic cycles. In a process, known as rectified diffusion, such bubbles collect gas from the liquid and grow in size. In the rarefaction cycle, the bubble radius increases and volatile gases or vapor can enter the bubble across the interface. In the following compression cycle, the bubble shrinks, and the diffusion of gases into the liquid is hindered by the smaller exchange surface. This effect is aided by the changing thickness of the liquid boundary layer, which generates high concentration gradients at large radii and small gradients in the compression phase. Rectified diffusion is responsible for the degassing of liquids under ultrasound, even at low sound pressure of 0.01 MPa. Such a growing bubble may reach the resonance radius, at which very strong oscillations cause surface instabilities and the generation of smaller bubbles. Surface oscillations are responsible for very high microstreaming in the vicinity of stable bubbles, which accelerates heat and mass transport. The behavior of some bubbles can change dramatically at a certain radius. The radius grows rapidly to more than twice the size in half an acoustic period. This is followed by a sudden collapse after which the bubble disappears. These bubbles are known as transient bubbles (Fig. (4)) and cause most of the sonochemical effects.

Transient bubbles have a very small collapse time which was first deduced by RAYLEIGH. An approximation for the collapse time in acoustic sound fields is

$$\tau_B = 0.915 \cdot R_{\max} \left( \frac{\rho_L}{p_m} \right)^{\frac{1}{2}} \left( 1 + \frac{p_v}{p_m} \right) \quad (9)$$

where  $R_{\max}$  is the maximum bubble radius before collapse,  $p_m$  the mean driving pressure (the sum of hydrostatic and sound pressure), and  $p_v$  the vapor or gas pressure inside the bubble at maximum expansion. Transient bubble generation is subject to two restrictions: First, a transient bubble must undergo extensive growth, for which its radius must exceed a certain threshold at which the forces acting on it are higher than the surface tension forces. Secondly, having reached this state, sufficient energy must be concentrated in a very short time, and this requires critical values of the radius before ( $R_{\max}$ ) and after collapse ( $R_{\min}$ ). Only in this case, are the energy dissipation (heat conduction, viscosity losses) smaller than the work done by the spherical convergence of the surrounding liquid. These two criteria are described by the so-called Blake threshold radius  $R_{B,0}$  and the Flynn dynamic radius  $R_{F,0}$ . Bubbles having initial radii  $R_0$  smaller than the Blake threshold and greater than the Flynn dynamic radius will undergo transient collapse. APFEL used these criteria and derived an expression for the maximum bubble radius before collapse.

$$R_{\max} = \frac{4}{3\omega} \left( \hat{p}_a - p_\infty \right) \sqrt{\frac{2}{\rho_L \hat{p}_a} \left( 1 + \frac{2}{3p_\infty} \left( \hat{p}_a + p_\infty \right) \right)}^{\frac{1}{3}} \quad (10)$$

Assuming isothermal expansion to maximum bubble radius  $R_{\max}$  and subsequent adiabatic collapse, the pressures and temperatures generated in a gas-filled transient cavity can be derived as

$$T_{\max} = T_0 (\gamma - 1) \left( \frac{R_{\max}}{R_0} \right)^3 \quad (11a)$$

$$p_{\max} = p_{g,m} \left( \frac{p_{\infty} (\gamma - 1)}{p_{g,m}} \right)^{\frac{\gamma}{\gamma - 1}} \quad (11b)$$

where  $p_{g,m} = p_{\infty} (R_0/R_{\max})^3$  is the pressure in the bubble at maximum radius.

### 2.2.3. Parameters Influencing Cavitation

Influencing parameters in sonochemical applications are listed in Table (2).

**Dissolved Gases** are present in most applications of ultrasound. The type and amount of these gases in the treated liquid are a very important factor for the sonochemical effects [11]. Highly gas saturated liquids have large numbers of cavitation nuclei and low cavitation thresholds. Degassed liquids need higher sound pressures for cavitation, but the sonochemical effects are in most cases more intense. The bubbles can collect gas from the surrounding liquid, and this rectified diffusion creates large bubbles with high gas contents. On collapsing, these bubbles create only moderate temperatures and pressures. As a general rule, degassing a liquid is always favorable in sonochemical applications. Beside the gas content of a cavitating bubble, the used gas is important (Table (3)). Gases with high polytropic exponents and small thermal conductivity show the best effects under sonication. Monoatomic gases like argon and xenon exhibit good cavitation intensities, whereas diatomic gases such as nitrogen and oxygen tend to decrease the observed effects. Gases with high thermal conductivity such as helium decrease the intensity of cavitation collapse to nearly zero.

**Vapor Pressure.** The vapor pressure of liquids can cushion the bubble collapse like a high gas content. Vapor in a transient bubble can be condensed in the compression cycle and lead to higher cavitation intensities than gas filled bubbles. Experiments with different solvents show that small vapor pressures are necessary for a sufficiently high cavitation intensity. Higher vapor pressures, especially near the boiling point of the liquid, can dampen the cavitation efficiency to nearly zero. If a substrate is subject to treatment within the collapsing bubbles, then a certain amount of its molecules must be present in the bubbles and exert an at least measurable vapor pressure. The existence of molecules inside the bubble can easily be proved by means of molecules which exist as ionic or molecular species at different pH values. Ionic species do not enter the bubbles, and high temperature pyrolysis products can therefore not be created.

**Viscosity.** High viscosity of a sonicated liquid increases the cavitation threshold markedly. Viscous liquids generate bubbles only at high sound pressures. Bubble motion is damped by the dissipative effect of the viscosity and the smaller maximum bubble radii, and the lower inward wall velocities terminate most sonochemical effects.

**Temperature.** The effect of temperature on sonochemical processes is explained by its influence on

viscosity, gas solubility, vapor pressure and surface tension. Any chemical reaction will be influenced by the temperature-dependent reaction rate coefficient. In most cases, cavitation is more pronounced at lower temperatures due to the lower vapor pressure of the liquid. This lowers the total gas content of the collapsing bubbles and causes higher cavitation intensities. This paradoxical temperature dependence is highly pronounced for sonochemical reactions involving radical generation in transient bubbles. Lesser effects are generally observed in heterogeneous systems, where intense micromixing by oscillating bubbles favors mass and heat transfer.

**Static Pressure.** The static pressure in a sound field alters the thresholds for rectified diffusion, transient bubbles and other characteristics. A high static pressure can prevent the generation of bubbles by ultrasound or create a different size distribution. For a given amount of energy, smaller bubbles with a higher energy content are created, which show very strong erosion activities in heterogeneous systems.

**Frequency.** The effect of frequency on sonochemical reactions is still an active field of research. Some measurements indicate that different frequency ranges are needed for special reaction types. Low frequencies in the range from 16 to 100 kHz, known as power ultrasound, are mainly active in heterogeneous systems with micromixing, cleaning, mechanical action on suspended solids and intense bubble motion. High frequencies favor high temperatures and pressures in the cavitation bubbles, thus creating a large number of radicals. The sonolysis of water seems to be most pronounced at frequencies between 300 and 500 kHz. Frequency is a very important parameter in defining whether a bubble of a given size is transient or stable. The smaller bubbles present in a high frequency sound field have a lower energy content than the larger bubbles generated at low frequencies. Beneficial for sonochemical effects is the higher number of cavitation events in high-frequency applications. In nearly all sonochemical processes, an optimum frequency can be found experimentally.

**Ultrasound Intensity.** The effect of intensity or power input to the ultrasonic device is complicated. Higher intensities provoke a larger amplitude at the vibrating surface in contact with the liquid. At low intensities, a linear dependency between generated sound pressure and amplitude is observed. Raising this intensity above the cavitation threshold of the liquid causes oscillating bubbles, and under certain circumstances the contact between radiating surface and liquid is lost. The motion of the transducer and the liquid are out of phase, an effect known as decoupling. A second reason for the nonlinear relationship between intensity and sonochemical effects is the creation of cavitation zones. Higher intensities create more and larger bubbles, which may coalesce and lead to less transient events. Energy efficiency and sonochemical effects are therefore sometimes smaller at higher intensities, and often the optimum intensity for a specific sonochemical effect must be determined experimentally.

**Pulsed Ultrasound.** Pulsed ultrasound is characterized by phases with and without ultrasound. In the ultrasound cycle, bubbles are created, grow by rectified diffusion, and may eventually collapse. The silent cycle can be used to remove larger bubbles by Archimedian forces. Smaller bubbles begin to dissolve, and the overall gas content decreases, giving optimum conditions for the next sonication cycle. Many sonochemical processes benefit from pulsed operation and show better performance than with continuous operation.

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## 2.3. Nonlinear Effects

### 2.3.1. Bubble Collapse near Boundaries

Undisturbed bubbles in liquids show spherical oscillations in a sound field [12]. Any extended disturbances such as boundaries, suspended solids, or reactor walls in the vicinity of the transient bubble prevent spherical collapse. Asymmetric bubble wall motion leads to the formation of an involution, which is directed towards the disturbance. In the late stages of the collapse of a transient bubble, a liquid microjet breaks through the remote bubble wall and impinges on the boundary. Liquid microjets can reach velocities in the range of several hundred meters per second and are responsible for cavitation erosion on solids. The pressures generated on solid surfaces can melt soft metals, create pitting, or disrupt inorganic layers on metals. A liquid jet with a diameter of roughly one tenth of the collapsing bubbles diameter creates a water hammer  $p_{WH}$  pressure of

$$P_{WH} = \frac{(\rho_L c_s \rho_T c_T) v_J}{\rho_L c_s + \rho_T c_T} \quad (12)$$

where  $c_s$  is the shock speed ( $c_s \approx c_L + 2v_J$ ),  $v_J$  the jet speed,  $c_T$  the speed of sound and  $\rho_T$  the density of the target. This pressure is maintained in the center of the jet for a time  $t_{col} = R_{max}/10c_s$  followed by a Bernoulli pressure of  $\rho_L v_J^2/2$ . Most heterogeneous reactions make use of these mechanical effects in cavitating sound fields. Even more intense effects are observed when clouds of bubbles collapse near solid boundaries. The concerted breakdown of such a hemispherical transient bubble cloud generates shock wave pressures and jetting with intensities some orders of magnitude higher than those of single bubbles [13].

### 2.3.2. Finite Amplitude Waves and Shock Waves

Most applications in ultrasound deal with rather small particle velocities  $v$ . This can be described by the acoustic Mach number  $M = v/c_L$ . A 20 kHz high-intensity step horn with an amplitude of 100  $\mu\text{m}$  creates a Mach number of about 0.01. For low Mach numbers, the acoustic approximation of incompressible liquids is applicable. In certain cases, for example focused sound fields, much higher Mach numbers are present and lead to distortion of the sinusoidal wave form. Density and sound pressure no longer satisfy a simple linear equation with a fixed speed of sound  $c$ . A pressure-dependent speed of sound is observed (material nonlinearity). Convective terms in the equation of motion cannot be neglected at higher Mach numbers and lead to a more complicated situation (convective nonlinearity) in which the real speed of the wave front consists of two parts, the speed

of sound  $c$  and the particle velocity  $v$ . The material nonlinearity and the convective nonlinearity tend to increase the propagation velocities of zones with high pressures. This leads to saw-tooth waveforms which develop a shock wave. Consisting of higher harmonics of the initial sound frequency, these saw-tooth waves are strongly attenuated and quickly decay into low-amplitude sinusoidal waves with the initial frequency. Shock waves are also formed in transient bubble collapse. If the bubble wall reaches high velocities, a shock wave is emitted into the surrounding liquid. The Mach number in this case is  $M = (dR/dt)/c_L$  and reaches values higher than unity. The shock wave is generated some distance from the bubble. Hickling and Plesset calculated, that above a pressure of 100 MPa inside the bubble, a shock wave starts at a distance of  $r/R_{\min} = 5-6$  where  $R_{\min}$  is the minimum bubble radius at collapse [14].

### 2.3.3. Streaming

**Acoustic Streaming.** As an acoustic wave travels through a medium, it can be absorbed. Because of the absorption of momentum in the direction of the sound field, flow is initiated in this direction. Local variations in intensity and energy absorption lead to local streaming velocities in the order of several centimeters per second. Finite amplitude waves create acoustic streaming due high absorption of higher harmonic components.

**Acoustic Microstreaming.** Small obstacles in a sound field create circulation by friction between their boundaries and the vibrating liquid particles. This acoustic microstreaming boundary layer has a thickness  $\delta_{MS}$  of

$$\delta_{MS} = \sqrt{\frac{2\eta_{L,S}}{\rho_L \omega}} \quad (13)$$

where  $\eta_{L,S}$  is the shear viscosity of the liquid. Microstreaming enhances mass and heat transfer and leads to shear forces on the obstacles.

### 2.3.4. Radiation Forces

Objects in an acoustic sound field experience a force whose magnitude and direction depends on the intensity of the source if the dimensions of the target are greater than the wavelength. Two types of radiation forces can be distinguished, depending on the boundary conditions. The Rayleigh radiation force acts on a target of area  $S$  in a closed vessel with energy density  $E$ :

$$F = 0.5(1 + \gamma)ES \quad (14)$$

The case of open vessels (free boundary condition) is treated by the Langevin radiation force

$$F = ES \quad (15)$$

which represents most experimental conditions. The Langevin radiation force is utilized to measure

the intensity of sound fields.

### 2.3.5. Bjerknes Forces

Stable oscillating bubbles experience translational radiation forces in a traveling-wave field. In standing-wave fields, these so-called primary Bjerknes forces act on oscillating bubbles and are due to a time-average force resulting from sound field pressure gradients and bubble oscillation. Bubbles below resonance size are attracted to pressure antinodes, whereas bubbles above resonance size travel down pressure gradients towards pressure nodes (Fig. (5)) [33].

Secondary Bjerknes forces arise when two oscillating bubbles are present in a pressure field. Attractive forces between bubbles with in-phase pulsation cause coalescence. Bubbles oscillating out of phase are repelled. The bubble oscillation is in phase when both bubbles are smaller or larger than resonance size and attractive forces dominate. If one bubble is smaller and one larger than resonance size, they oscillate in out of phase and repel one another.

Primary and secondary Bjerknes forces lead to structures known as cavitation streamers. A large bubble above resonance size oscillating with surface instabilities and located in a pressure node generates microbubbles below resonance size, which are repelled and forced towards the pressure antinode of a standing-wave field, where attractive forces cause clouds of oscillating microbubbles. The lines of microbubbles are often called microstreamers.

### 2.3.6. Forces on Small Particles

Small particles with radii smaller than the cavitation bubbles are accelerated in the velocity and pressure gradients around oscillating bubbles. These forces are even greater when particles are subject to shock waves. Particle velocities of up to 500 km/h can be reached. On collision of two such particles, oxide layers are removed and metals are melted together. Such treated metals are used in catalysis, where activity enhancements by a factor of up to  $10^6$  are observed.

Like the Bjerknes forces, solid particles whose acoustic properties differ from those of the liquid are subject to primary and secondary forces. Primary forces drive particles into pressure nodes, where secondary forces between particles are responsible for further aggregation [15].

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## 2.4. Sonochemical Effects

The effects of ultrasound on chemical reactions are in most cases secondary effects caused by cavitation and can be divided into five main groups:

- 1) Reactions inside the cavitation bubble at high temperatures and pressures
- 2) Reactions at the gas – liquid interface of the bubbles (secondary reactions of products formed within the bubbles, high-temperature reactions of nonvolatile liquids)
- 3) Reactions due to high pressures in the surrounding liquid
- 4) Effects caused by nonlinear bubble collapse near boundaries
- 5) Enhanced mass and heat transfer by macro- and micromixing

### 2.4.1. Hot-Spot Theory

Very high temperatures and pressures are generated in a cavity on collapse. Nolting and Neppiras calculated temperatures of up to  $10^4$  K in a transient cavity. This would lead to black-body thermal radiation which can be observed spectroscopically. Temperatures of 5000 K in the bubble, 2000 K in the liquid boundary layer and pressures of 50 MPa were found in experiments with metal carbonyles [5]. UV/Vis spectroscopy of the cavitating liquid showed good agreement with the thermal spectra of carbon and the metals at the same temperature. Thus, by creating extreme temperatures in transient bubbles and the surrounding liquid boundaries, high-temperature reactions can be initiated in a liquid that remains at ambient temperature. These calculations are confirmed by the presence of pyrolysis products of irradiated liquids. These include the homolytic cleavage of water, the cleavage of carbon-halogen bonds, and the production of radical products from organic liquids like alkynes and alkenes. The extreme heating and cooling rates of about  $10^5$  K/s resemble those in the freezing of molten metals when poured onto a plate with a temperature of  $-270$  °C. Under the extreme conditions of a transient bubble, even plasma reactions or fusion were proposed. Theoretically, conditions similar to those on the surface of the sun are possible.

### 2.4.2. Shock Wave Theory

The compression of transient bubbles leads to an increasing bubble wall velocity which may eventually reach the speed of sound of the liquid. In true transient cavitation, the bubble vanishes after collapse, creating a shock wave in the liquid. Particles and macromolecules are accelerated in the steep pressure gradient and are shock fragmented. High speed particles collide and undergo mechanical damage.

### 2.4.3. Supercritical Water Theory

High temperatures and pressures in aqueous sonochemistry may lead to conditions under which

supercritical water is likely. Supercritical water is known to have a strong solvent action towards organic compounds and extreme chemical activity. Sonochemical effects are possible inside the supercritical water layer surrounding a transient bubble. At the time being, no direct evidence for the generation of supercritical water in ultrasound fields has been found experimentally.

#### 2.4.4. Charge Theory

Russian workers questioned the existence of true cavitation and postulated a somewhat different sonochemical effect. Oscillating bubbles undergo very rapid size changes. Friction forces at the gas-liquid bubble boundary can create charged species which can lead to secondary chemical reactions in the bulk liquid.

#### 2.4.5. Promotion of Single Electron Transfer

Classical ionic bimolecular nucleophilic substitution reactions ( $S_N2$ ) have been interpreted as a radical mechanism with radical formation by transfer of a single electron according to



Ultrasound has an accelerating effect on such single-electron transfer reactions (SETs) and can alter the reaction pathways when ionic  $S_N2$  reactions and SET reactions occur simultaneously and lead to different products.

#### 2.4.6. Cleaning

Microstreaming, shock waves, and liquid microjets in the vicinity of solid surfaces lead to very efficient cleaning. This effect has been used in industry for more than forty years. Insoluble layers of inorganic salts, polymers, or liquids can be removed by ultrasonic cleaning effect. In heterogeneous systems such a clean reactive surface leads to improved dissolution rates of metals in acids and enhanced reaction rates. Chemical reactions giving insoluble products are freed from these mass transport limiting layers and react rapidly.

#### 2.4.7. Mechanical Activation

Several mechanisms for the activation of solids in chemical reactions are induced by the mechanical effects of ultrasound and transient cavities. High intensity ultrasound is able not only to remove passivating layers on solids, but to break solids like salts and metals as well (Fig. (6)).

**Surface Renewal.** Impacting liquid microjets or shock waves create the pitting on solid surfaces [17]. These indentations are free of unreactive layers and react readily with dissolved reactants. Mechanical energy is introduced to the lattice of the solid and leads to slightly excited active

centers. In general, such activated solids exhibit higher reaction rates than the untreated solids.

**Particle Disruption.** Brittle solids can be cleaved by transient cavities. Like in milling operations, this leads to higher specific surfaces, high energy content at the disrupted site, and reactive fresh surfaces. Because of the tiny bubble size, very small particles in the micrometer range can be produced.

**Particle Agglomeration.** Acceleration of small particles in the shock wave field of a transient bubble can lead to particle agglomeration. Highly accelerated particles collide and melt together on contact. Contact temperatures of nearly 3000 K were measured for very small particles. Particle agglomerates in the vicinity of transient bubbles are fragmented and yield higher specific surfaces [16]. Primary and secondary forces on suspended solids can increase the amount of aggregation in pressure antinodes of a standing wave field. These effects are used, for example, in separation processes.

## 2.4.8. Enhanced Mass and Heat Transfer

Many heterogeneous reactions are accelerated by the enhanced micromixing properties of cavitating sound fields. Oscillating and transient bubbles create intense microstreaming in the vicinity of suspended solids. Macromixing is induced by acoustic streaming and the oscillation of bubbles in the sound field. In most cases, a locally different mass transport coefficient is observed. Tenfold increases in mass-transfer coefficients compared with silent reactions were measured [18].

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## 3. Heterogeneous Systems

### 3.1. Solid–Fluid Reactions

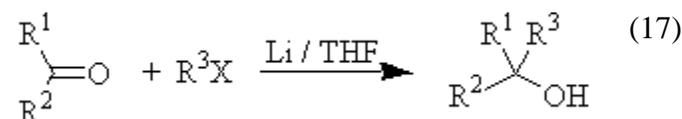
In heterogeneous solid–fluid reactions, asymmetrical bubble collapse creates shock waves and liquid microjets. These are responsible for particle fragmentation, pitting, and cleaning of the solid. Particles that are larger than the transient cavity must be present to induce asymmetrical collapse. Powdered solids which are smaller than the transient bubble are accelerated in the shock waves surrounding a cavity. High impact speeds lead to cleaning, shock fragmentation and mechanical activation. Metal particles in the micrometer range are melted together. Only tungsten (*mp* 3410 °C) resists aggregation by welding [19]. In a 20 kHz sound field for example, extended particles have to

be roughly 200  $\mu\text{m}$  in size to perturb the radial collapse. In this case, loss of material and some surface hardening of metals is observed. Surface hardening is due to an increasing lattice deformation with higher defect density on the surface of the solid. This high defect density also leads to a better chemical reactivity for specific reactions and facilitates syntheses by solid–fluid reactions, especially in organometallic chemistry.

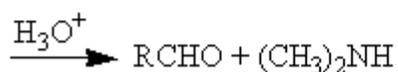
### 3.1.1. Noncatalytic Reactions

**Alkali metals** are often used in synthesis and are very suitable for ultrasonic processes [8]. Passivating layers on the pure metals are removed, and the induction times of reactions are shortened dramatically. Aromatic radical anions like naphthalene–lithium, anthracene–sodium or biphenyl–sodium are easily formed under ultrasound [9] in 45 min, compared to 48 h without ultrasound. Very fine dispersions of sodium and potassium are possible in solvents with low vapor pressures such as toluene or xylene. Dispersed colloidal metals are used in Dieckmann condensations and Wurtz coupling.

The Barbier reaction needs under classical conditions dried solvents like THF or ether, an organic chloride, and lithium wire or powder [20]. With ultrasound, moist solvents can be used. A reduction of induction time, high reaction rates and high selectivity are observed because sonication is performed under mild conditions below the boiling point of the solvent. In most cases, no difference in the total yield was observed. One of the advantages of the Barbier reaction is the possibility to produce highly unstable intermediates in situ which will react with a second reagent:

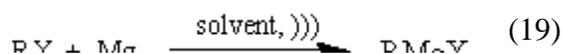


The Bouveault Reactions of alkyl, cycloalkyl, and aryl bromides with Li and DMF in ether solvents to form aldehydes is drastically enhanced by ultrasound, and high selectivity is observed [8]:

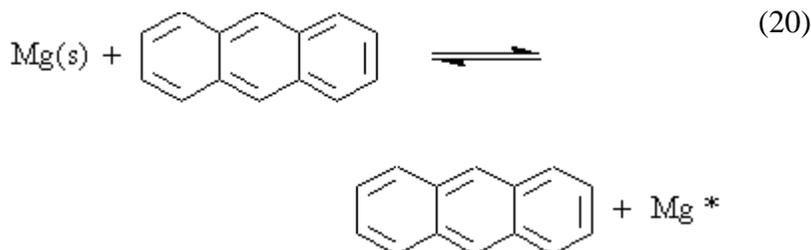


This special case of a Barbier reaction shows no reaction at an ultrasonic frequency of 50 kHz in diethyl ether, but reasonable yields at 500 kHz. This unexpected frequency effect can not be explained by cavitation and remains one of the open questions of sonochemistry.

**Magnesium** is used widely in the synthesis of Grignard reagents. Fast reactions and virtual absence of induction times under sonication allow safe and easy production of these valuable intermediates [21], [22].



Sonication experiments on 2-bromobutane revealed a 60-fold increase in reaction rate even in impure wet ether [23]. Bogdanovic et al. developed a method to prepare a highly reactive magnesium-anthracene complex. Using this activated magnesium  $Mg^*$ , a variety of Grignard reagents can be produced:



Grignard reagents are often used for transmetalation reactions to prepare less readily accessible organometallic compounds such as organoboranes and organozinc compounds.

**Aluminum.** Improvements in reaction rate and yield have been reported for the preparation of alkyl aluminum halides. An interesting result was the reaction of bromoethane with Al in THF to give ethylaluminum sesquibromide under ultrasound, which is not observed under stirring conditions.

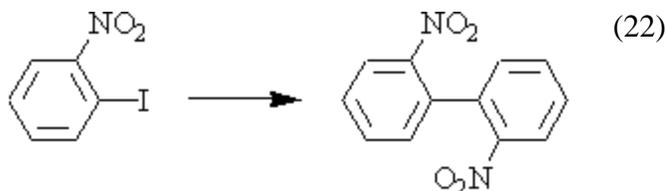
**Zinc.** The direct formation of organozinc compounds from zinc and halides is possible, but transmetalation with Li is more reliable:



The Simmons-Smith cyclopropanation of alkenes with diiodomethane or dibromomethane and Zn benefits from ultrasound. Whereas under ultrasound 98% yield after 2 h of irradiation are measured, only 50% yield is possible in the stirred reaction.

A sonochemical variant of the Reformatsky reaction for the synthesis of  $\beta$ -hydroxyesters or  $\beta$ -lactams has been reported to give excellent yields compared to traditional methods using activated zinc or cosolvents. Allylations of carbonyl compounds can be performed in an  $H_2O/THF/Zn$  slurry. Substantial rate enhancements are observed in the dehalogenation of aryl halides with zinc in aqueous HMPA with nickel(II) chloride. Cross coupling of perfluoroalkylzinc reagents with halides is possible.

**Copper.** Copper can be activated in an acoustic field to allow reaction at moderate temperatures. The Ullmann coupling reaction requires high temperatures. Sonicated copper is fragmented and cleaned to give highly reactive fresh surfaces and a 64-fold increase in reaction rate:



**Nonmetals.** In most reactions of nonmetals suspended in a liquid phase, the solid phase serves as one of the reagents and is consumed. Low solubility and slow reaction rates are common. Under ultrasound, a quasihomogeneous mixture is created by intense particle fragmentation and high mass transfer coefficients. Strong bases like KOH or NaOH are readily fragmented and undergo very fast and selective reactions. Oxidations of alcohols with potassium permanganate in benzene do not

need water as a cosolvent under sonication. ANDO et al. [7] were able to activate manganese dioxide in a pre-sonication process to give a material which oxidizes several alcohols. Quite unusual reductions of heteroatom-halogen bonds have been reported. Lithium aluminum hydrides are used to substitute aromatic halides in excellent yields.

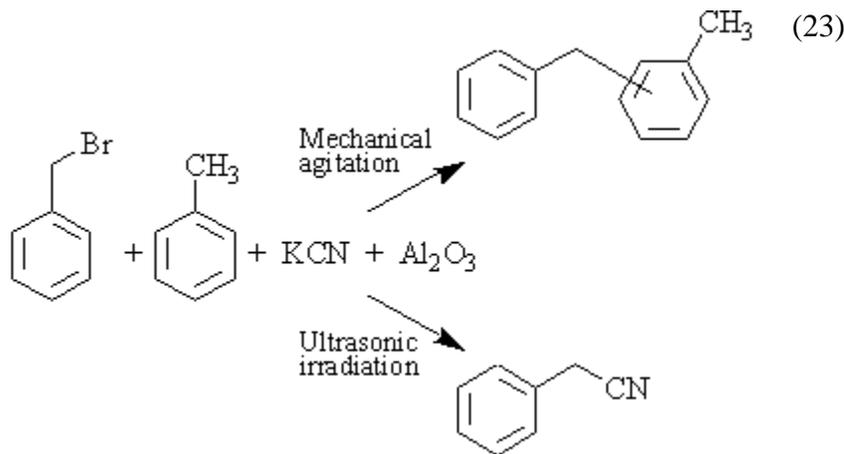
CONTAMINE et al. [34] examined the Michael addition of a diethyl malonate anion to the double bond of phenyl styryl ketone. Solid KOH is used to promote the reaction in toluene. Two rate-limiting steps, the formation of a carbanion and its addition to the double bond, which is interpreted as a single electron transfer (SET), are likely. Under ultrasound, very fast reaction is observed and explained by enhanced mass transfer and KOH fragmentation, removing the first limiting step, and the influence of ultrasound on SET reactions.

### 3.1.2. Catalytic Reactions

**Catalyst Preparation.** Sonication has been applied to the preparation of catalysts for a wide range of processes. Hydrogenation catalysts like Pd/C, Pt/C, and Rh/C show better reactivity after mechanical activation and higher specific surface areas due to cleavage of the support. These activated catalysts are used in hydrogenation of alkenes, acetophenone, methylstyrene, and fat hardening. A remarkable increase in activity was found by SUSLICK [25], who sonicated Ni powder for up to 1 h in 1-octene. The metal showed a very clean surface (removal of Ni oxide) and a  $10^5$ -fold activity, like freshly prepared Raney Ni, but a smaller specific surface area after prolonged sonication due to agglomeration.

Unusual catalysts are prepared by sonication of solutions of metal carbonyls in alkanes. Fe, Ni, Co, and Mo carbonyls give nanostructured amorphous metal or metal carbide powders.

**Sonicated Catalytic Reactions.** Inorganic supports like alumina, silica gel, and zeolites promote nucleophilic substitution with alkali metal cyanides in organic solvents. ANDO et al. [26] discovered the sonochemical switching of a reaction pathway in the reaction of benzyl bromide with potassium cyanide and alumina in toluene. While stirring leads to a mixture of the Friedel-Crafts products, benzyltoluenes, ultrasonic irradiation promoted nucleophilic substitution to give benzyl cyanide. It was concluded, that cyanide had poisoned the active Lewis acid sites, therefore decreasing the catalytic activity of the alumina.



Hydrogenations of alkenes by formic acid or hydrazine and palladium-carbon with in situ

generation of hydrogen have been reported [9]. Commercial applications such as the hydrogenation of soybean oil and fat hardening in three-phase processes have already found industrial utilization.

### 3.1.3. Precipitation and Crystallization

Applications of ultrasound in crystallization and precipitation lead in most cases to a narrower particle size distribution and therefore to improved material properties [3]. Supersaturated or supercooled solutions of materials to be crystallized are often seeded to give a narrow particle size. Because seeding is normally nonuniform, broad size distributions with uneven crystal sizes and shapes are produced. High-power ultrasound promotes and improves nucleation and growth of crystals by cavitation bubbles, the disruption of seeds, and the breakage of larger crystals. There is some evidence that the sonication of supersaturated solutions leads to creation of highly uniform nucleation sites by disturbing the metastable equilibrium. The enhanced micromixing avoids nonuniform concentration gradients in the solution. Industrial applications are found in the frozen food industry, where even seeding prevents the disruption of cellular materials on freezing. Enhanced crystallization has been applied to molten metal to obtain fine grain sizes and fewer gaseous inclusions with the aim of obtaining very good mechanical properties of the cast alloy.

### 3.1.4. Atomization

The production of atomized sprays from a liquid is facilitated by the use of ultrasonic devices. Normally, sprays are produced by forcing high-velocity liquids through a small aperture. Blockage and nonuniform size distributions are often observed. The initial velocity of the produced spray tends to form clusters. Ultrasonic devices make use of high velocity changes on a vibrating tip. The particle size can be controlled by either the frequency or the intensity of the ultrasonic horn. Materials like molten glass or metal are easily atomized, show a very narrow size distribution, and have a very low particle velocity.

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## 3.2. Ultrasonic Extraction

Ultrasonic extraction processes from biological cells, bacteria, microorganisms, or plants are used in research as well as on an industrial scale [5]. Cell disruption, enhanced micromixing, and

impregnation of material by liquid microjets reduces processing time and allows less harmful solvents to be used for extractions. The normally lower temperatures allow very mild processing with high yields of alkaloids, essential oils, glycosides, and fragrances.

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### 3.3. Liquid–Liquid Reactions

Only a few examples of the influence of ultrasound on liquid-liquid reactions have been reported in the literature. Most of them benefit from the emulsifying effect of ultrasound and the resulting high interfacial area. In some cases, a phase-transfer catalyst became unnecessary. Most reactions are between immiscible aqueous and organic liquid phases.

The decomposition of organic halides is faster due to the better mass transfer from the organic phase into the aqueous phase, where secondary radical reactions with hydroxyl radicals lead to unspecific degradation. Examples of ester hydrolysis, substitution reactions, and addition reactions in two phase liquid-liquid systems can be found in [7].

**Ultrasonic Mixing.** Nonreactive mixtures of liquids can be mixed by ultrasound. High shear velocities and oscillating and transient bubbles create very intense local conditions, which are employed for homogenization or emulsification. Many industrial processes in the food and drug industries use the liquid whistle, a long-known device which uses a high-velocity liquid stream impacting a steel blade to create vibrations. Typical applications are the homogenization of water-oil mixtures for the production of soups, sauces or the rapid mixing of fruit juices from concentrates [3].

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### 3.4. Phase-Transfer Catalysis

Alkylations are important reactions in heterocyclic chemistry and provide a simple means for introducing substituents. Phase-transfer catalysis (PTC) allows very fast and facile reactions when combined with sonication. The alkylation of indole and carbazole with alkyl and benzyl halides under liquid/solid PTC conditions in toluene with solid KOH gives higher yields and shorter reaction times than the stirred reaction [20]. Reaction times are shortened from several hours to less than one hour under ultrasound.

The preparation of azides from primary alkyl halides and aqueous sodium azide under PTC conditions is easier and cheaper under ultrasound and smaller amounts of PTC reagents can be used.

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### 3.5. Sonoelectrochemistry

**Deposition of Metals.** Acoustic microstreaming and transient events can aid the deposition of metals in electroplating processes [27]. The very high mixing efficiency in cavitating sound fields is used to destroy the polarization barrier surrounding the electrode. Constant mechanical treatment by transient bubbles leads to surface hardening, less porosity, better brightness and to very good adhesive deposits for a variety of metals, including copper and gold.

**Electro-Synthesis.** Electrochemical methods are of widely recognized importance in the generation of intermediates which are difficult to prepare by other means [24], [28]. Problems arise due to mass transfer limitations, fouling of the electrode, or the evolution of gases. Applications in the Kolbe reaction and dechlorination of polychlorinated biphenyls can be found. Reductions of benzaldehyde and benzoquinone are reported in [29], in which a novel electrochemical reactor employs the ultrasound source as one electrode for the reaction. The production of microemulsions and the dispersing effects of ultrasound are used where immiscible liquids have to be treated. Applications are found in wastewater treatment and other environmentally important processes. An effective removal of gases produced at an electrode can help to shift reversible reactions. Chlorine and hydrogen removal leads to very effective electrochemical cells. Transient bubbles and intense micromixing are responsible for the disintegration of diffusion layers, thus eliminating mass transfer limitations in electrochemical reactions. Cyclovoltammogrammic measurements of reversible redox reactions show very characteristic peak shapes in the silent case due to diffusion limitations. Under sonication, step responses are observed, and the underlying electrode kinetics can be measured without mass transfer limitations. Limiting currents which are ten times higher than in the silent reaction are common. Due to the profound influence of ultrasound on electrode kinetics, a change in the product spectrum of electrochemical reactions is sometimes observed.

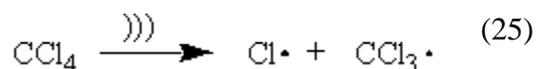
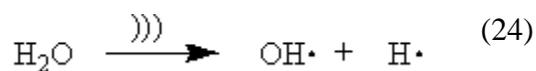
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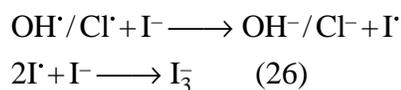
## 4. Homogeneous Systems

### 4.1. Aqueous Liquids

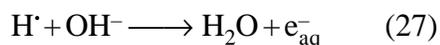
The sonochemistry of water, often called sonolysis, is mainly determined by the production of radicals. Among the earliest observations in sonicated aqueous solutions was the liberation of molecular iodine from solutions of KI. The so-called Weissler Reaction is one of the standard reactions for the chemical dosimetry of cavitating liquids. The primary step is the homolytic cleavage of water in the bubble. Saturating the water with tetrachloromethane facilitates the production of radicals:



Hydrogen radicals react with water molecules to give further OH<sup>•</sup> radicals and molecular hydrogen. The recombination of OH<sup>•</sup> radicals at the bubble-liquid interface forms hydrogen peroxide. VON SONNTAG [30] estimated the OH<sup>•</sup> concentration in the liquid boundary layer to be  $1.2 \times 10^{-2}$  mol/L. Hydroxyl radicals and chlorine radicals react with iodine to yield after recombination molecular iodine as a complex with I<sup>-</sup>:



The existence of hydrated electrons under noble gases has been proposed by Margulis [6].



Volatile components in the water enter the cavitating bubble and are attacked by the OH<sup>•</sup> radicals. Dissolved gases like nitrogen yield HNO<sub>2</sub>, HNO<sub>3</sub>, and smaller amounts of NH<sub>3</sub> and N<sub>2</sub>O. Mixtures of N<sub>2</sub> and H<sub>2</sub> lead to the production of NH<sub>3</sub>; mixtures of H<sub>2</sub> and CO lead to formaldehyde. A mixture of N<sub>2</sub> with CO, CH<sub>4</sub>, or HCHO gives small amounts of various amino acids.

Organic components are attacked by OH<sup>•</sup> and H<sup>•</sup> radicals within the bubble or in the bulk liquid to give a wide range of secondary radical products. The irradiation of aqueous solutions of maleic acid with traces of Br<sub>2</sub> leads to a rapid isomerization to fumaric acid. The reaction is initiated by the cleavage of the bromide bond, the addition of the bromide radical to the double bond of maleic acid. Isomerization and subsequent liberation of bromide radicals lead to fumaric acid, which precipitates. The degradation of organic solutes in water is used in the wastewater treatment for

removal of traces of halogenated aromatic and aliphatic compounds.

Inorganic compounds also undergo secondary radical reactions. Redox reactions with various ionic components are reported in [7].

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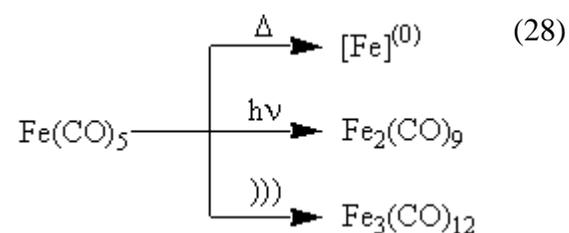
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## 4.2. Nonaqueous Liquids

Most nonaqueous liquids have a much higher vapor pressure than water, and this strongly cushions the transient bubble collapse. Therefore, early measurements that showed only very few sonochemical effects in water-free liquids are easily understood. Such liquids exhibit sonochemical effects such as bond cleavage only at low ambient temperatures. The sonolysis of alkanes [31], for example, yields nearly the same products ( $H_2$ ,  $CH_4$ , 1-alkenes) as the high-temperature pyrolysis reaction. On irradiation halocarbons undergo homolytic halogen-carbon bond cleavage and give molecular chlorine and secondary radical products.

Another example for the preparation of organometallic complexes and the different product spectrum compared to thermolytic or photolytic pathways was presented by SUSLICK who sonicated iron pentacarbonyl in alkanes:



The products are decomposed to pyrophoric iron, when cavitation becomes too intense, and only solvents with higher vapor pressure and therefore less intense transient cavitation are suitable.

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## 4.3. Polymers and Macromolecules

The preparation and degradation of long chain molecules under sonication is the result of two effects: creation of radicals by mainly mechanical chain cleavage of polymers and initiation of radical reactions by generation of primary radicals in transient bubbles.

**Depolymerization.** Early experiments with sonicated macromolecules revealed decreasing viscosity of the solutions. These changes can be attributed to a homolytic chain cleavage of the molecules. Drag forces acting on a dissolved polymer molecule are created in the vicinity of oscillating bubbles. High stresses are also created in shock waves from transient cavities. In dilute solutions, the polymer radicals react with solvent molecules to terminate the radical chain reaction. In concentrated solution, copolymerization and side chain branching occur. A lower limit for the molecular mass of the degraded polymer is observed in most cases. At a sufficiently small chain length, further degradation is stopped by the small drag forces acting on the molecule. The limiting molecular masses lie in the range of  $10^4$ . The mechanical action of transient cavitation in polymer degradation becomes clear in the resulting molar mass distributions. Chains of higher mass are degraded more rapidly than those of lower mass. Degradation by ultrasound therefore leads to a narrower size distribution. Controlled depolymerization can be used to improve material properties such as mean polymer molecular mass, viscosity, and workability [3].

**Polymerization.** The creation of radicals in transient bubbles can be used to initiate radical polymerizations. Very high initial polymerization rates are observed at low temperatures for both pure monomers and monomers with initiators. Ultrasound produces a large number of radicals compared to traditional methods, and highly uniform size distributions are possible. With further sonication, depolymerization becomes increasingly important, and proper control of ultrasound parameters is necessary to achieve the desired polymer properties. The emulsification capabilities of ultrasound are utilized in suspension polymerization, where less surfactant is required and smaller size distributions are observed.

**Copolymerization.** The chain cleavage of polymers generates radicals which react with other reactants in the bulk. Concentrated polymer solutions (above 10 wt %) show side branching and copolymerization if two different polymers are present. Copolymerization of two polymers, for example, polystyrene and poly(methyl methacrylate), by ultrasound leads to random block and graft copolymers. In most cases the product is unfavorable, but the method can be a valuable tool for the preparation of mixtures from immiscible polymers. Copolymerization of a polymer in the presence of monomers leads to better defined block copolymers.

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## 4.4. Sonoluminescence

Ultrasonic irradiation of liquids produces under certain instances light. This sonoluminescence is easily observed in water, ethylene glycol, and glycerin. In water, light emissions at 310 nm from excited  $\text{OH}^\cdot$  radicals and a broad band in the entire continuum are observed. Whether this broad emission is due to black body radiation or excited molecules is still unknown. Other liquids show emission spectra from different excited species. Alkanes show a strong band in the  $\text{C}_2^*$  region (the Swan band). The production of  $\text{C}_2\text{H}_2$  from sonicated alkanes provides evidence for excited species in the transient cavity. Sonochemically excited molecules and their reactions in the high-temperature region of bubbles seem to be responsible for the flame-chemistry-like behavior of sonoluminescence.

**Single Bubble Sonoluminescence.** In single-bubble sonoluminescence (SBSL) experiments [5], a bubble is trapped in a pressure antinode of a standing wave field. At a sufficiently high sound pressure of slightly above 0.1 MPa, this bubble oscillates stably but with high wall velocities and emits light in the UV/Vis region. Higher sound pressures cause a transient behavior and disappearance of the bubble. SBSL is used to examine the various parameters that influence bubble motion and sonochemical sonoluminescence efficiency.

**Multi-Bubble Sonoluminescence.** In extended sound fields, several types of bubbles, (e.g., stable and transient), are present. These create different temperatures and pressures inside oscillating bubbles and should therefore show a broader spectrum than in SBSL. MBSL experiments with aqueous solutions of various alcohols revealed a scavenging effect of these compounds. Sonoluminescence was suppressed at higher concentrations of alcohol, and this was interpreted in terms of reaction with  $\text{OH}^\cdot$  and  $\text{H}^\cdot$  radicals produced by homolytic water cleavage. Electrolytes can alter the SL spectrum. Emissions of neutral metal atoms indicate the possibility of metal vapor inside the cavities, which show the characteristic bands in the compression cycle when temperatures are high enough to vaporize the metals [5]. The mechanism of the generation of metal atoms from ionic metallic atoms by cavitation is still unknown, but theories about the reduction of the metal ion at the hot solid–liquid interface of a transient cavity seem plausible.

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## 5. Equipment

### 5.1. Transducer Technology

Ultrasound transducers create the high frequency vibrations which are submitted into the liquid.

Two major types of transducers are used for liquids: liquid-driven and electromechanical.

*Liquid-driven transducers* are widely used in the food industry for mixing and homogenization. The principle is that of a liquid whistle. Liquid is pumped through a small orifice and hits a blade. The sudden pressure drop in the orifice causes hydrodynamic cavitation, and the blade generates ultrasonic vibrations and cavitation. A precise design of flow velocities, orifice and blade are necessary to allow high liquid throughputs with optimum mixing conditions.

*Electromechanical transducers* are based on piezoelectric or magnetostrictive principles. Both transducers need a high frequency generator for electrical supply. Magnetostrictive transducers are made of ferromagnetic material which alters its geometrical dimensions in an applied magnetic field. Bars or rods made of ferrite ceramics achieve high driving forces below 100 kHz. The major drawback of magnetostrictive transducers are their poor efficiency and rather broad frequency behavior.

Piezoelectric materials change their dimensions when charges are applied to opposite faces. These transducers have a natural resonance frequency at which the driving current produces the highest efficiency. Piezoelectric transducers are often made of barium titanate, lead metaniobate, and lead zirconate titanate ceramics and are supplied in most laboratory and industrial equipment. Operation at highest efficiency is responsible for the fixed frequency of common ultrasonic systems and the reason for the difficulty in examining the influence of frequency on sonochemical effects. Modern piezoelectric transducers have a sandwich structure with two electrically opposed piezo ceramics between two metal blocks. The sandwich is clamped together to prevent mechanical damage due to stress in the ceramic. The transducer usually has a length of half a wavelength, operates in compression mode, and generates amplitudes of up to 20  $\mu\text{m}$  [32]. Piezoelectric transducers are depicted schematically in Figure (7).

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## 5.2. Reactors for Sonochemical Reactions

One of the major drawbacks in industrial applications of ultrasound is the complex scale-up procedure. Readily available laboratory equipment such as ultrasonic baths, high-intensity disintegrator horns, and cup horn reactors are used to measure sonochemical effects. All influencing parameters such as intensity, frequency, temperature, and vessel geometry must be the same for reproducible results. Critical ultrasonic parameters include the amplitude of the transducer, the ultrasonic intensity, the total power input, the specific power input per volume, the gas content, the local sound-energy distribution, and, in the case of heterogeneous reactions, the distribution of reactants. A successful scale-up must take these various factors into account.

## 5.2.1. Laboratory Equipment

Low-intensity applications can be tested in a commercial ultrasonic bath (Fig. (8) a). Several transducers are mounted at the bottom of a bath and are driven with the same frequency. A complicated standing wave field is created, and the sonochemical effects depend on the location of the samples in the bath and the filling height.

Probe systems are applicable in high intensity experiments at up to ca. 100 W/cm<sup>2</sup> at frequencies below 100 kHz. Multiplication of the transducer amplitude by a booster and a horn make it possible to increase the amplitude by a factor of around 10. The vibrating tip of the horn is dipped into the liquid and creates intense cavitation in its vicinity (Fig. (8) b). Ultrasound is attenuated rapidly, and only a few centimeters are sonochemically active. Such probes generate a large amount of streaming, so external stirring is unnecessary. The intense cavitation causes erosion of the tip and therefore contamination of pure liquids. A variant of the probe system is the so-called cup-horn reactor with indirect sonication of a submersed sample through a sound-transmitting liquid, which can be cooled (Fig. (8) c).

## 5.2.2. Large-Scale Equipment

Liquid-whistle reactors (Fig. (9) a) are still very important in homogenization and mixing processes. High throughput, stable operation, and the ability to adapt to existing flow systems are only some of the advantages of this system [23]. Fruit juices, sauces, and mayonnaise are prepared in large quantities. This low-intensity equipment can not be used where more severe cavitation is required. Other low-intensity devices are reactors with external or submersed plate or rod transducers (Fig. (9) b, c) which are easily fitted to existing tanks of several cubic meters and allow a fast scale-up. Tube transducers can also be retrofitted to existing plants. All low-intensity devices transmit sound energy over large volumes with dimensions greater than the liquid wavelength. The typical power input is roughly 50 W per transducer at a frequency of 20 kHz and a diameter of 6 cm.

High-intensity devices are applicable when the dimensions of the sonicated volume are equal to or smaller than the liquid wavelength. Probe systems can be used in small flow cells, which consist of several probes in series and can be retrofitted to existing plant. Gap reactors force liquids through the most active zone of a probe transducer. The power input per transducer reaches 2 kW with a radiating surface diameter of up to 10 cm.

Another way to introduce high-intensity ultrasound are tube reactors (Fig. (10)). Transducers are mounted on the outer wall of a tube and create intense cavitation in the center. Variants of this principle include the cylindrical pipe reactor; the cylindrical reactor with core cooling; hexagonal and heptagonal tubes, which allow easier transducer mounting on their plane walls; the Branson sonochemical reactor with a coupling fluid between the horn and the reactor wall; and the Sodeva sonitube with a stepped horn and a resonant collar mounted on a cylindrical pipe.

Gap reactors (Fig. (11) a) consist of a high-intensity stepped horn which is coupled with a small gap of a few millimeters. The fluid is driven through the gap and is treated by high-intensity ultrasound for a very short time. Particle size reduction and mixing are the main applications for these devices.

The reverberatory ultrasonic reactor (Fig. (11) b) consists of two opposing plates with a gap of a few

centimeters. The use of two different frequencies (20 and 15 kHz) is very effective in particle size reduction. Other high-intensity systems are implemented in a tube (Fig. (11) c, d). Radial oscillations are responsible for the transmission of sound into the liquid. Examples for these devices are the Martin-Walter push-pull reactor and the Telsonic rod-reactor.

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### Sonochemistry - Table 1

Applications of ultrasound in processing

Field	Applications
Heterogeneous reactions	activation of solids in reactions, fragmentation, dispersion, agglomeration, preparation of catalysts, hydrogenation at room temperature
Homogeneous reactions	generation of radicals, oxidation of wastewater compounds, nanoparticle synthesis
Polymer processing	controlled degradation, initiation of polymerization, copolymerization, mixing in suspension polymerization
Electrochemistry	avoidance of mass transport limitations, electrode fouling, change in reaction pathways
Cleaning	cleaning of items in aqueous and nonaqueous media
Mixing	dispersion of solids, particle agglomerates, and pigments; mixing of immiscible liquids
Crystallization	initiation of seeding, control of particle size distribution, control of material properties
Extraction	fast and mild extraction of essential oils or microbiological material
Welding	welding of thermoplastics and metals
Cutting	cutting of ceramics and metals
Separation	improved filtration, agglomeration, and separation of particles

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### Sonochemistry - Table 2

Important influencing parameters in sonochemical applications

Parameter	Property	Effect
Dissolved gas	polytropic ratio	cavitation intensity
	thermal conductivity	primary sonochemistry
	solubility	cavitation intensity
Vapor pressure	content of bubbles	cavitation intensity
Liquid viscosity	dissipative effects	cavitation intensity
Temperature	liquid properties	cavitation intensity
	thermal activation	secondary reaction rate
Static pressure	thresholds	cavitation intensity and
	gas solubility	extent of cavitation zone

Frequency	thresholds	cavitation intensity
	wavelength	extent of cavitation zone
Intensity	thresholds	cavitation intensity
	attenuation	extent of cavitation zone
	maximum bubble radius	cavitation intensity

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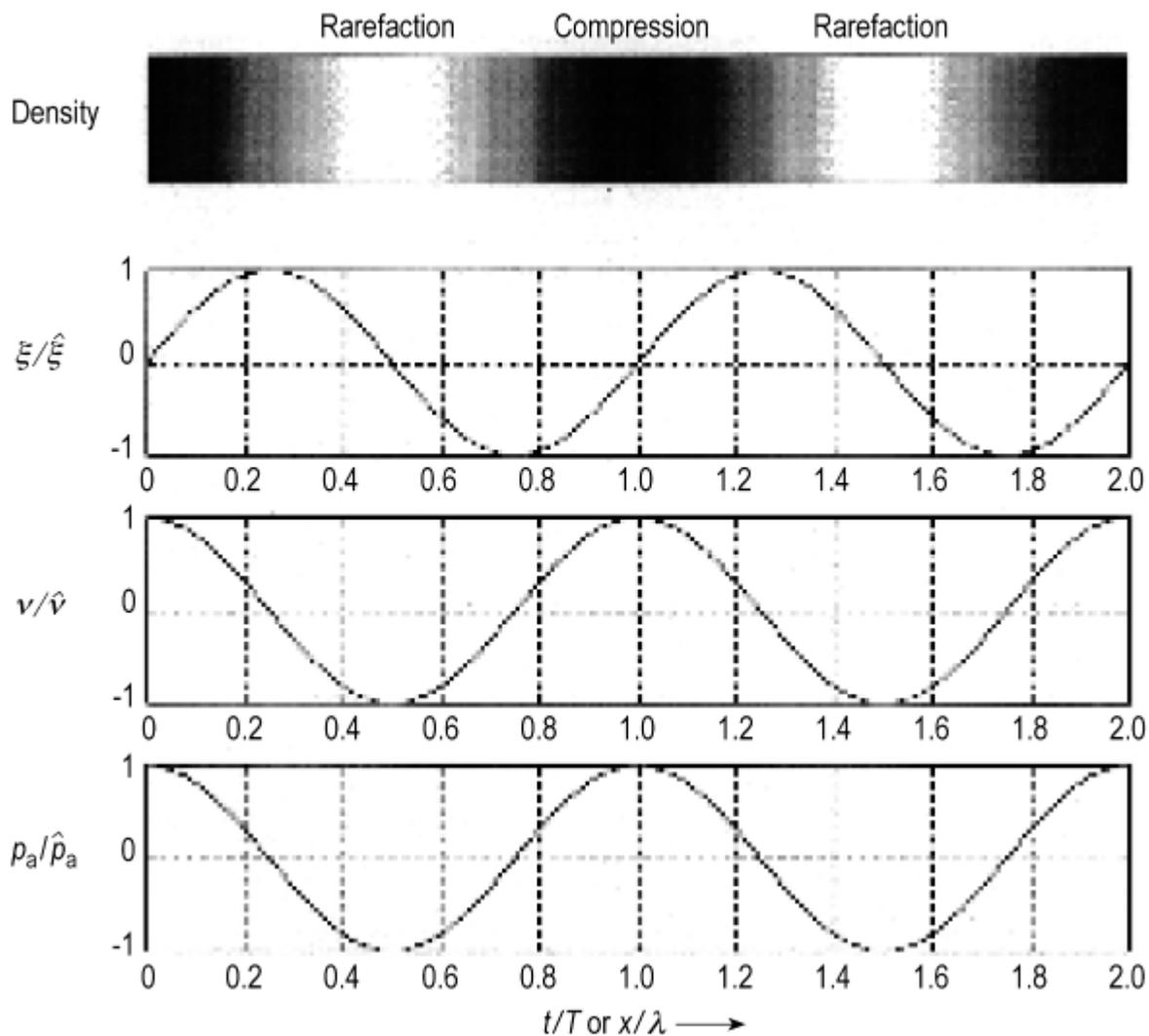
### Sonochemistry - Table 3

Properties of different gases and their influence on H<sub>2</sub>O<sub>2</sub> yield and sonoluminescence intensity

Gas	Specific heat ratio $\gamma$	Thermal conductivity, mWm <sup>-1</sup> K <sup>-1</sup>	Solubility in water at 20 °C, mL/100 mL H <sub>2</sub> O	Relative H <sub>2</sub> O <sub>2</sub> yield [11]	Relative sonoluminescence intensity [5]
Nitrogen	1.40	25.83	2.33	2.5	45
Oxygen	1.40	26.46	4.89	13.5	35
Helium	1.65	149.68	0.94	1	1
Neon	1.67	48.02	2.6	7	18
Argon	1.67	17.75	5.6	21.5	54
Krypton	1.67	9.46	11.0	24.0	180
Xenon	1.67	5.19	24.1	27.5	540

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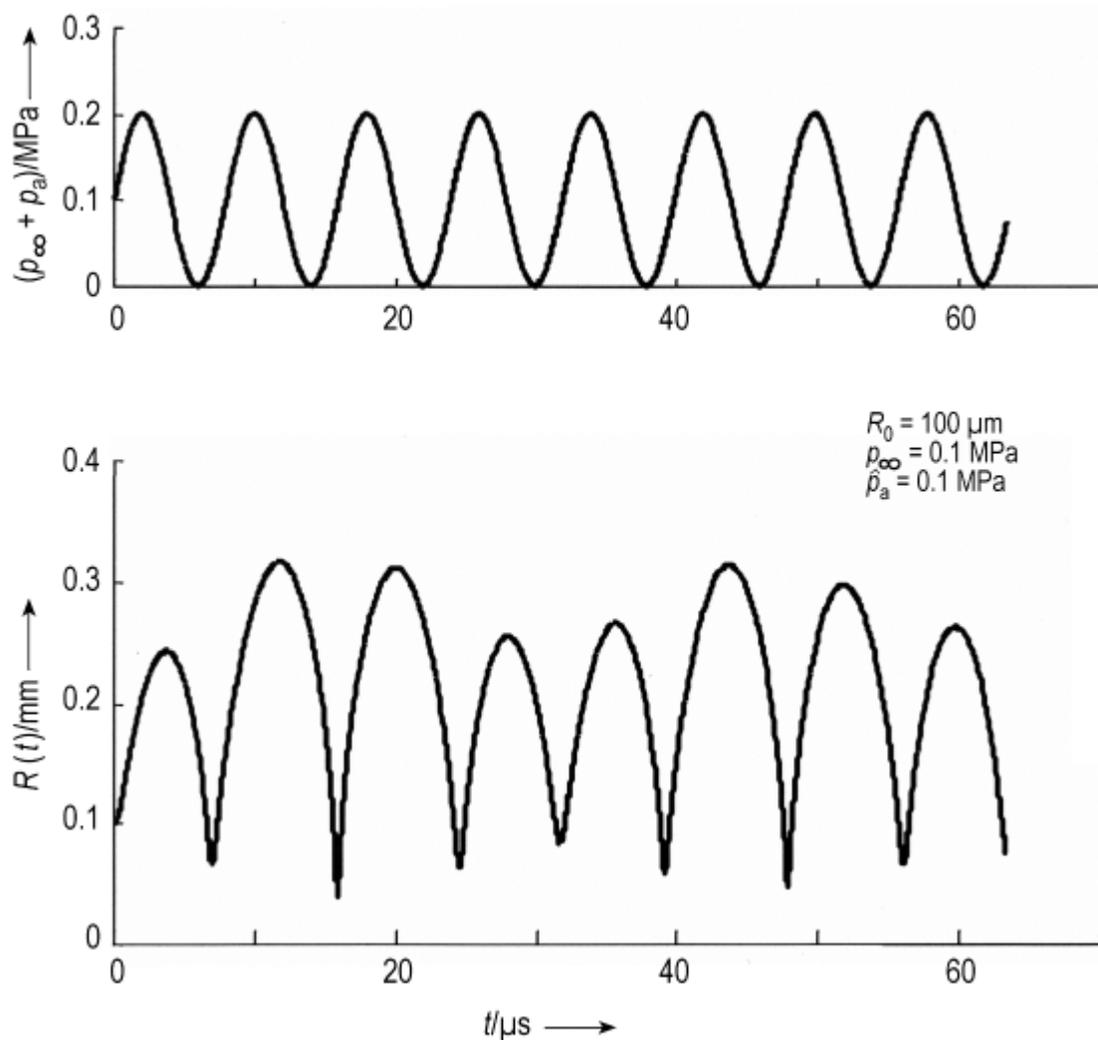
### Sonochemistry - Figure 1



Propagation of a traveling wave with density, normalized particle displacement, particle velocity and sound pressure as a function of normalized time or coordinate

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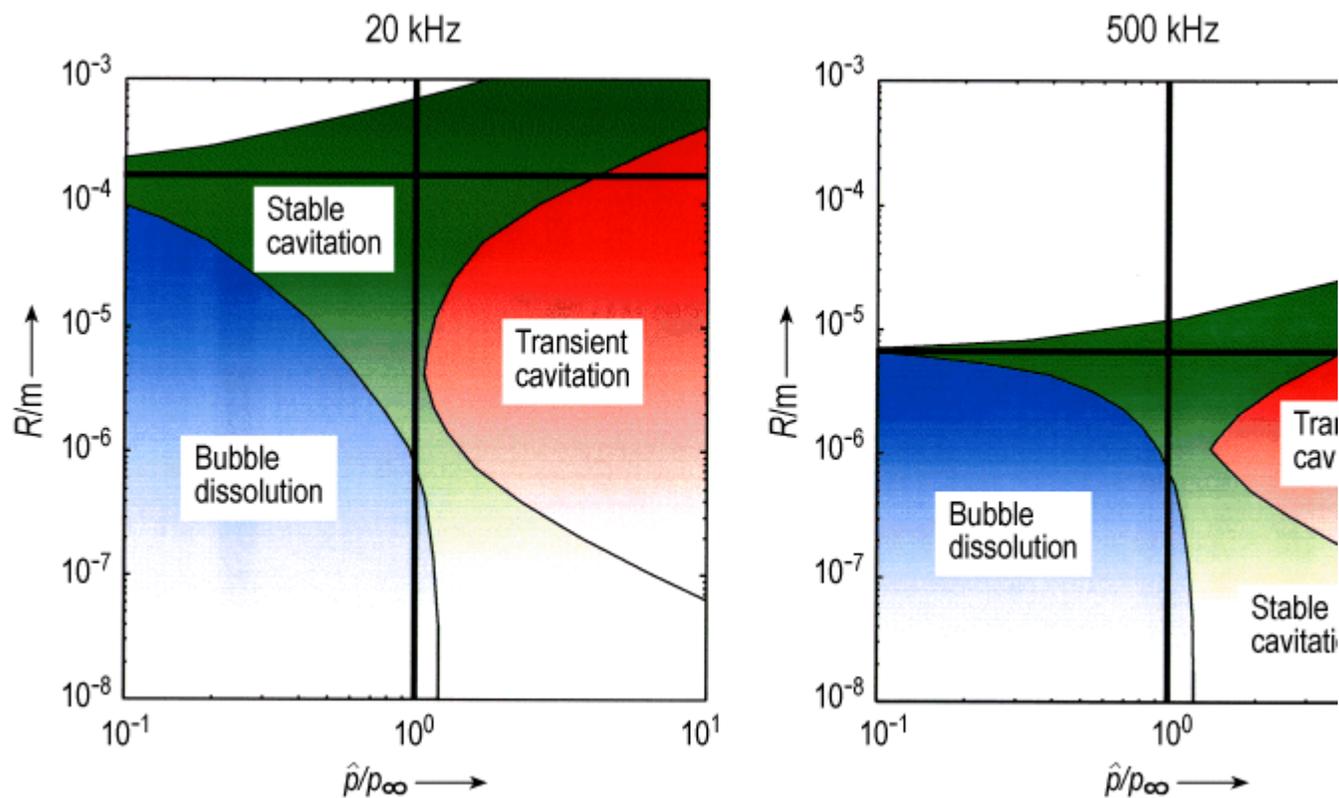
## Sonochemistry - Figure 2



Total pressure (top) and solution of the Rayleigh–Plesset equation for bubble radius (bottom) of a stable bubble as a function of time for air saturated water at 20 kHz with an initial bubble radius  $R_0$  of 0.1 mm, a static pressure of 0.1 MPa and a sound pressure of 0.1 MPa

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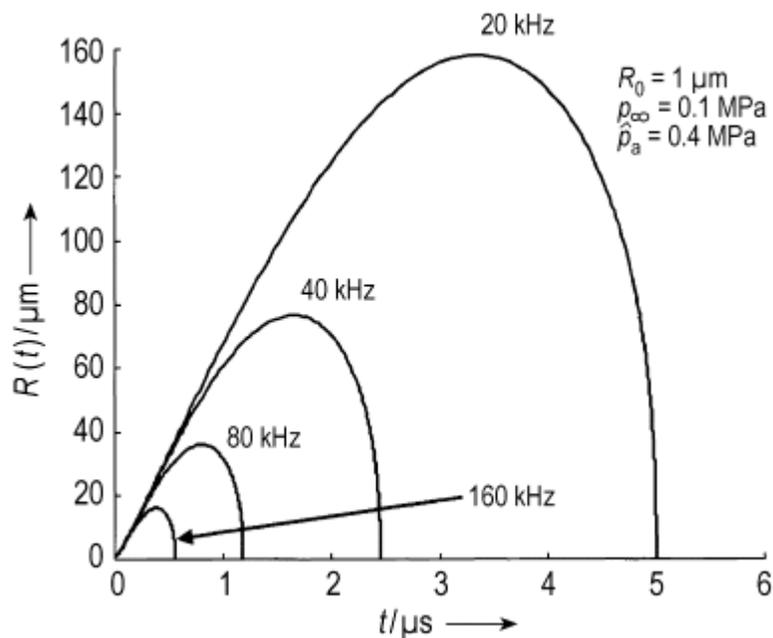
Sonochemistry - Figure 3



Simplified cavitation thresholds and regions for air saturated water at a static pressure of 0.1 MPa at frequencies of 20 and 500 kHz

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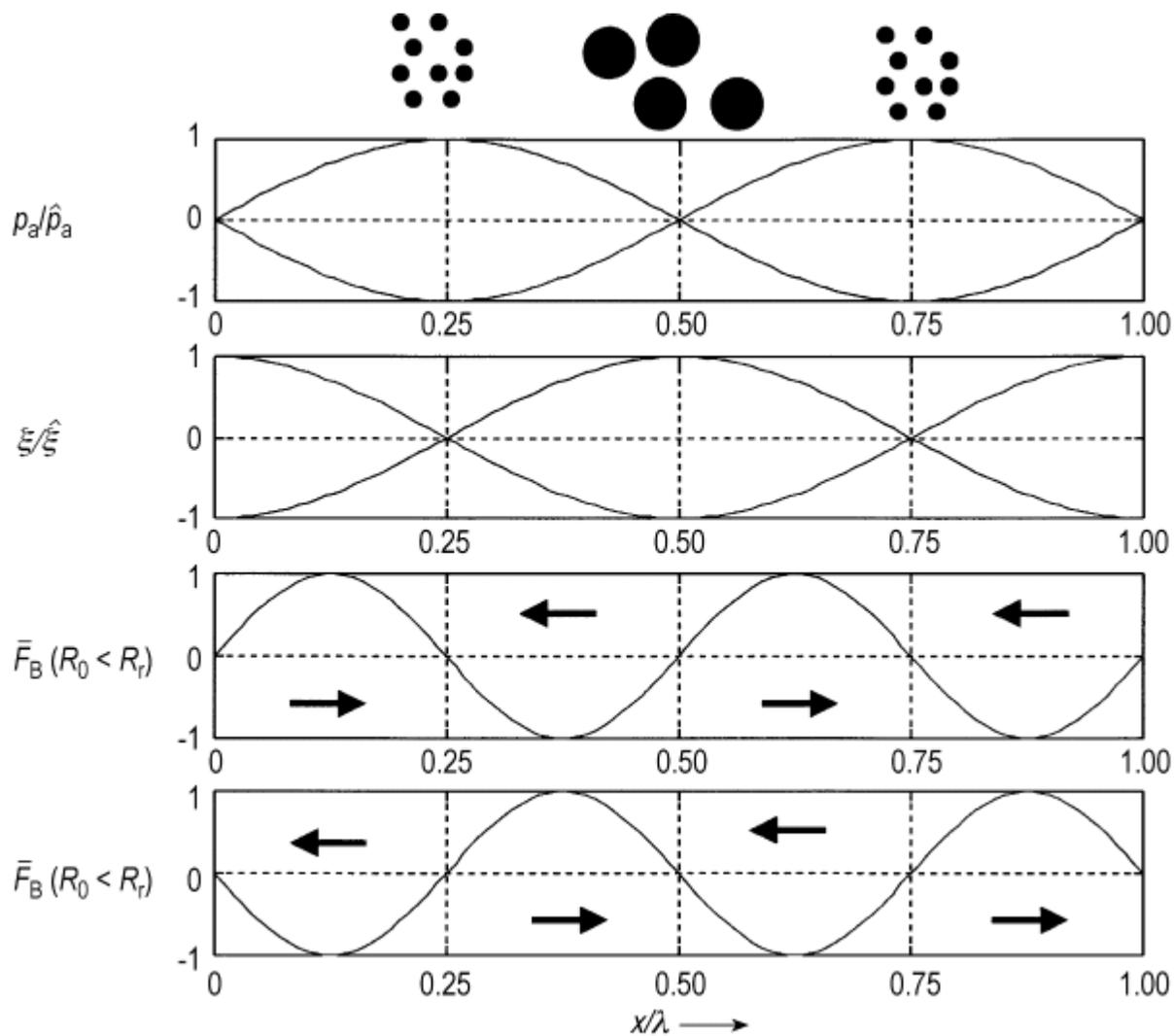
#### Sonochemistry - Figure 4



Bubble radius as a function of time for a transient cavity with an initial radius of  $R_0 = 1 \mu\text{m}$ , a static pressure of 0.1 MPa, and a driving sound pressure amplitude of 0.4 MPa in air-saturated water. The maximum bubble radius decreases with increasing frequency

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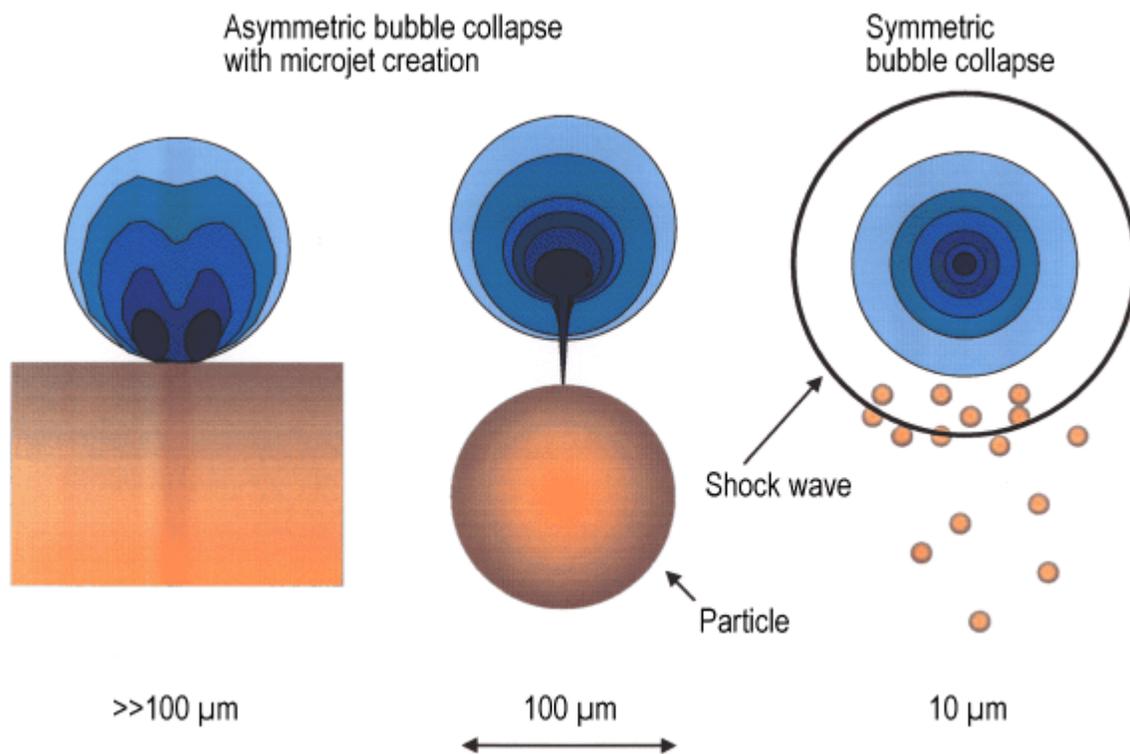
**Sonochemistry - Figure 5**



Normalized sound pressure, particle displacement and primary Bjerknes forces acting on bubbles smaller and greater than the resonance radius  $R_0$ . Small bubbles collect in pressure antinodes (displacement nodes), whereas large bubbles travel toward pressure nodes

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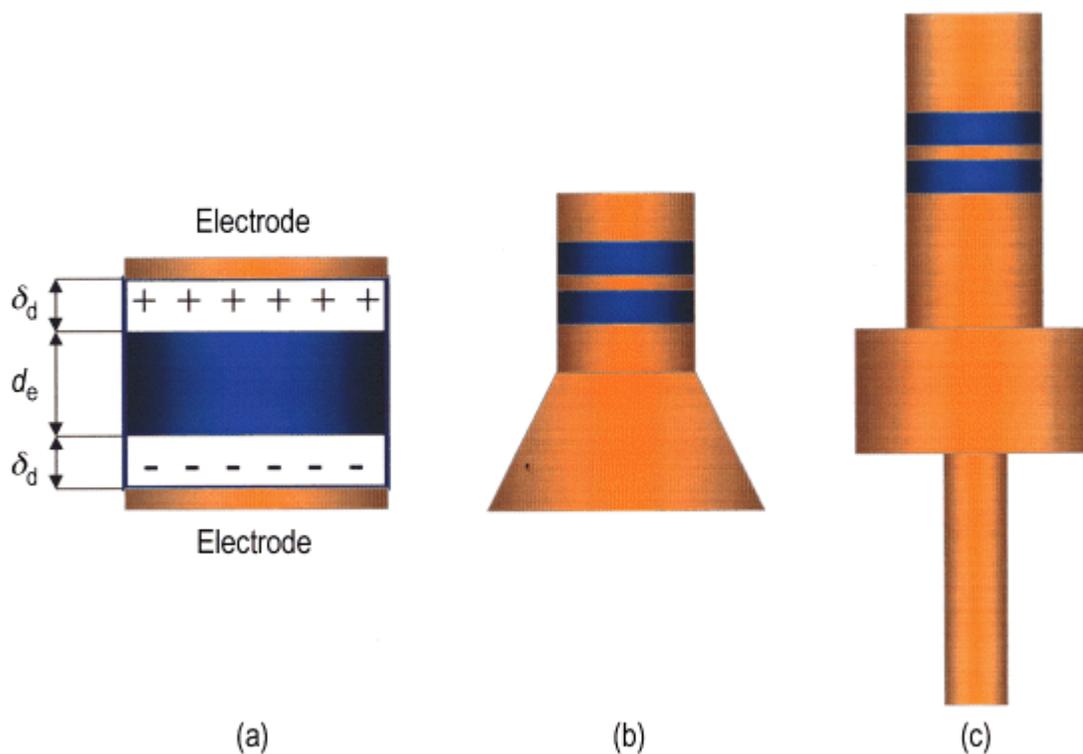
Sonochemistry - Figure 6



Influence of transient bubbles on particles of different size in a 20 kHz sound field. Extended surfaces lead to asymmetrical collapse with formation of microjets. Medium-sized particles to less asymmetrical collapse. Small particles are accelerated by bubble oscillation and in the shock wave

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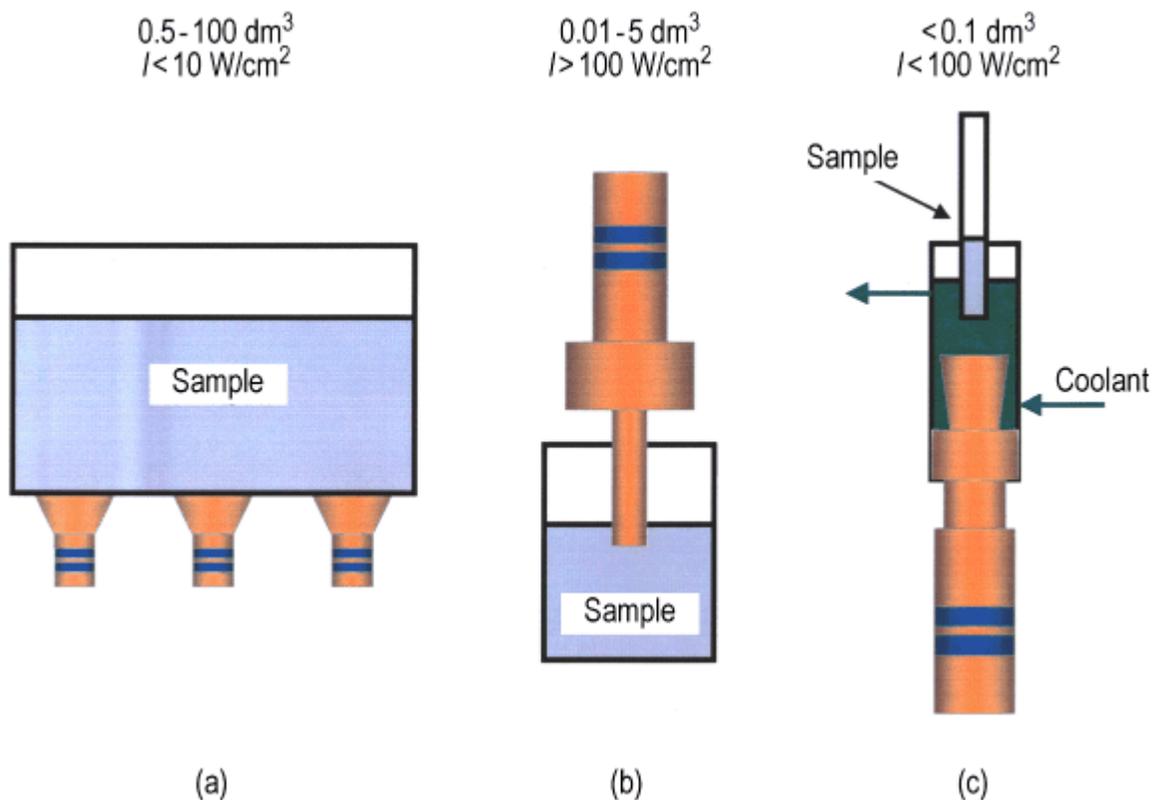
Sonochemistry - Figure 7



a) Schematic sketch of a piezoelectric ceramic with electrodes which changes its thickness  $d_e$  with applied charge; b) Transducer sandwich with two piezoceramics for low intensity devices; c) Transducer with booster and stepped horn

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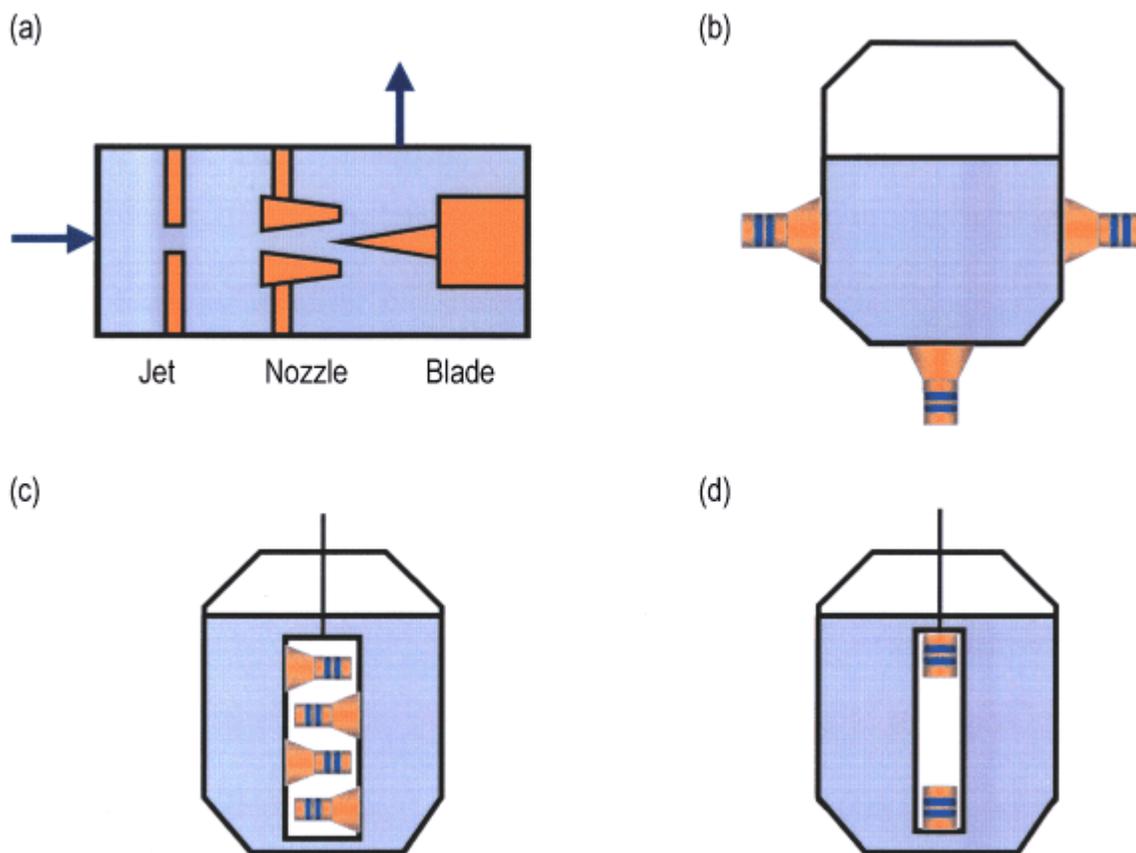
Sonochemistry - Figure 8



Laboratory equipment for sonochemical experiments a) Ultrasonic bath; b) direct-immersion horn; c) Cup-horn reactor

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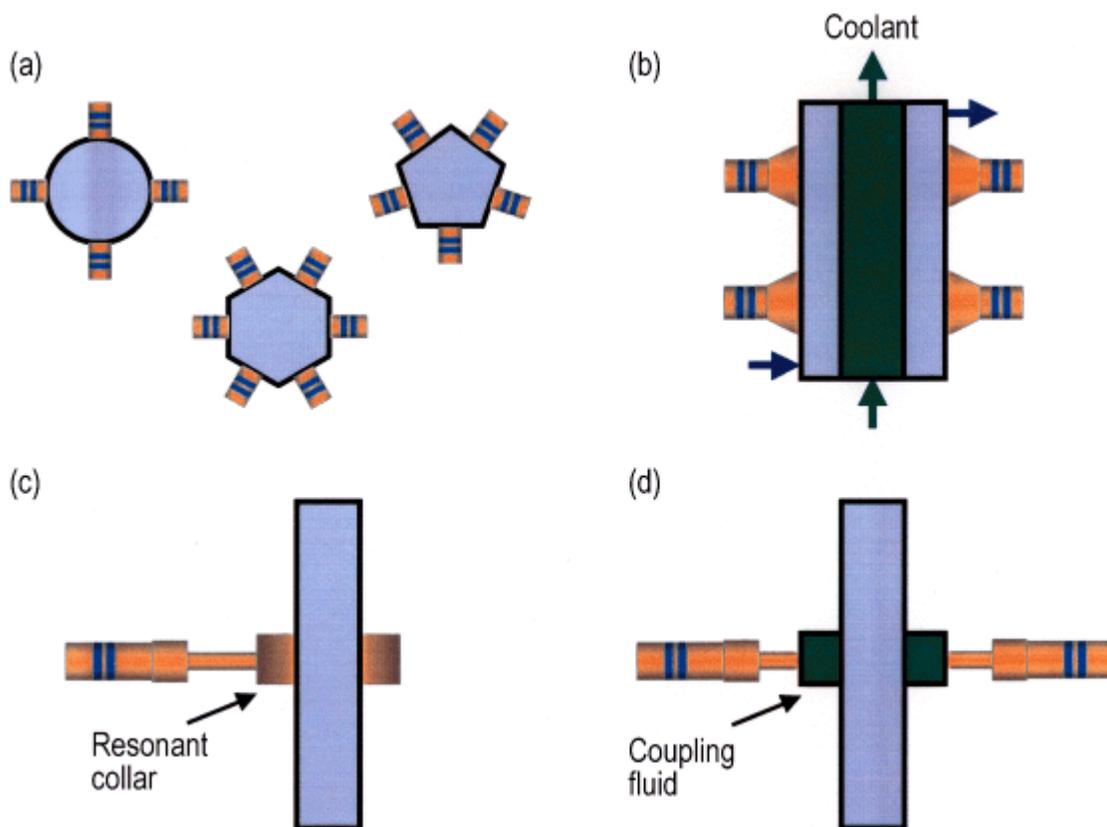
### Sonochemistry - Figure 9



Low-intensity ultrasonic devices a) Liquid whistle; b) Tank reactor with wall-mounted transducers; c) Tank with submersed plate transducer; d) Tank with submersed rod transducer

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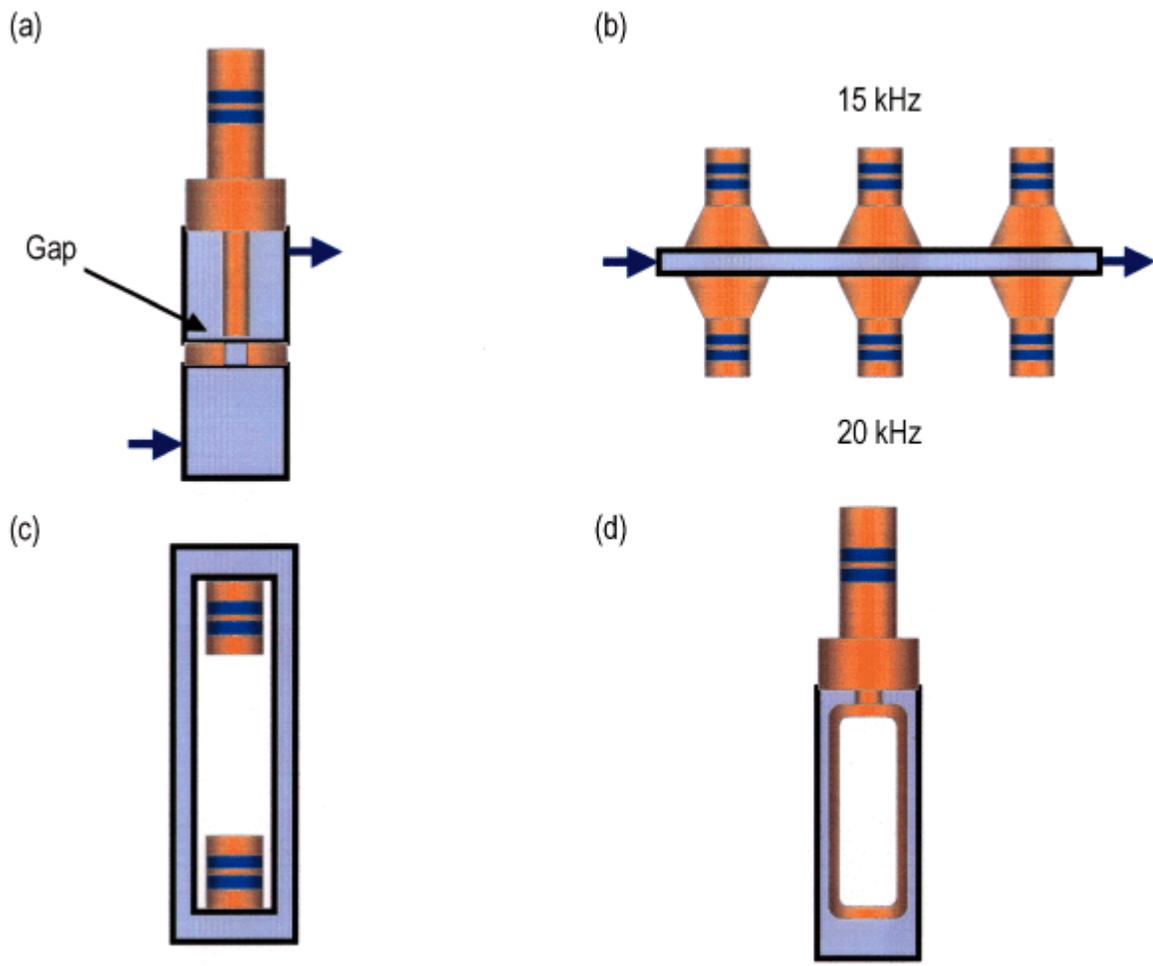
### Sonochemistry - Figure 10



Tube reactors a) Conical, hexagonal, and heptagonal reactors; b) Raiganis tube reactor with axial cooling; c) Sodeva sonitube with stepped horn and resonant collar; d) Branson sonochemical reactor with coupling fluid

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### Sonochemistry - Figure 11



a) Gap reactor; b) Lewis reverberatory ultrasonic reactor; c) Martin Walter push-pull reactor; d) Telsonic rod reactor