

THE SONOCHEMISTRY CENTRE AT COVENTRY UNIVERSITY

'The Home of Sound Science'

INTRODUCTION To SONOCHEMISTRY

1. **ULTRASOUND**

- 1.1 HISTORICAL BACKGROUND
- 1.2 THE POWER OF SOUND
- 1.3 REFERENCES

2. **ACOUSTIC CAVITATION**

- 2.1 HOMOGENEOUS LIQUID-PHASE REACTIONS
- 2.2 CAVITATION NEAR A SURFACE
- 2.3 HETEROGENEOUS POWDER-LIQUID REACTIONS
- 2.4 REFERENCES FOR CAVITATION

3. **TRANSDUCERS**

- 3.1 GAS-DRIVEN TRANSDUCERS
- 3.2 LIQUID-DRIVEN TRANSDUCERS
- 3.3 ELECTROMECHANICAL TRANSDUCERS
 - 3.3.1 Magnetostrictive Transducers
 - 3.3.2 Piezoelectric Transducers
 - 3.3.3 Low frequency vibrating bar transducer system

4. **REACTOR DESIGN AND SCALE UP**

- 4.1 BATCH TREATMENT
- 4.2 FLOW SYSTEMS
- 4.3 REFERENCES

5. **EXAMPLES OF RESEARCH PROJECTS**

1. ULTRASOUND

If you were asked what you knew about ultrasound you would almost certainly start with the fact that it is used in animal communications (e.g. bat navigation and dog whistles). You might then recall that ultrasound is used in medicine for foetal imaging, in underwater range finding (SONAR) or in the non-destructive testing of metals for flaws. A chemist would probably not consider sound as the type of energy that could be used for the excitation of a chemical reaction. Indeed up to a few years ago the use of ultrasound in chemistry was something of a curiosity and the practising chemist could have been forgiven for not having met the concept. To increase chemical reactivity one would probably turn towards heat, pressure, light or the use of a catalyst. And yet, if one stops for a second to consider what is involved in the transmission of a sound wave through a medium it is perhaps surprising that for so many years sound was not considered as a potential source of enhancement of chemical reactivity. The only exception to this being the green-fingered chemist who, in the privacy of his own laboratory, talks, sings or even shouts at his reaction. After all, sound is transmitted through a medium as a pressure wave and the mere act of transmission must cause some excitation in the medium in the form of enhanced molecular motion. However, as we will see later, in order to produce real effects the sound energy must be generated within the liquid itself. This is because the transfer of sound energy from the air into a liquid is not an efficient process.

1.1 HISTORICAL BACKGROUND

The basis for the present-day generation of ultrasound was established as far back as 1880 with the discovery of the piezoelectric effect by the Curies [1-3]. Most modern ultrasonic devices rely on transducers (energy converters) which are composed of piezoelectric material. Such materials respond to the application of an electrical potential across opposite faces with a small change in dimension. This is the inverse of the piezoelectric effect. If the potential is alternated at high frequencies the crystal converts the electrical energy to mechanical vibration (sound) energy – rather like a loudspeaker. At sufficiently high alternating potential high frequency sound (ultrasound) will be generated.

The earliest form of an ultrasonic transducer was a whistle developed by Francis Galton (1822-1911) in 1883 to investigate the threshold frequency of human hearing [4]. A diagram of the whistle is to be found in the section on transducers. Galton himself was a remarkable man. As well as inventing the whistle that carries his name he explored and helped map a portion of the African interior, invented the weather map and developed the first workable system for classifying and identifying fingerprints. His whistle was part of his study of sensory perception, in this case to determine the limits of hearing in terms of sound frequencies in both humans and animals.

The first commercial application of ultrasonics appeared around 1917 and was the first “echo-sounder” invented and developed by Paul Langévin (1872-1946). He was born in Paris and was a contemporary to Marie Curie, Albert Einstein and Hendrik Lorentz. He was noted for his work on the molecular structure of gases, analysis of secondary emission of X-rays from metals exposed to radiation and for his theory of magnetism. However Langévin is more generally remembered for important work on piezoelectricity and on piezoceramics. The original “echo-sounder” eventually became underwater SONAR for submarine detection during World War 2. The transducer was a mosaic of thin quartz crystals glued between two steel plates (the composite having a resonant frequency of about 50 kHz), mounted in a housing suitable for submersion. The early "echo sounder" simply sent a pulse of ultrasound from the keel of a boat to the bottom of the sea from which it was reflected back to a detector also on the keel. For sound waves, since the distance traveled through a medium = $1/2 \times \text{time} \times \text{velocity}$ (and the velocity of sound in seawater is accurately known) the distance to the bottom could be gauged from the time taken for the signal to return to the boat. If some foreign object (e.g. a submarine) were to come between the boat and the bottom of the seabed an echo would be produced from this in advance of the bottom echo. In the UK this system was very important to the Allied Submarine Detection Investigation Committee during the war and became popularly known by the acronym ASDIC. Later developments resulted in a change in the name of the system to SONAR (**SO**und **N**avigation **A**nd **R**anging) which allowed the surrounding sea to be scanned. The original ASDIC system predated the corresponding **RA**dio **D**etection **A**nd **R**anging system (RADAR) by 30 years.

Essentially all imaging from medical ultrasound to non-destructive testing relies upon the same pulse-echo type of approach but with considerably refined electronic hardware. The refinements enable the equipment not only to detect reflections of the sound wave from the hard, metallic surface of a submarine in water but also much more subtle changes in the media through which sound passes (e.g. those between different tissue structures in the body). It is high frequency ultrasound (in the range 2 to 10 MHz) which is used primarily in this type of application because by using these much shorter wavelengths it is possible to detect much smaller areas of phase change i.e. give better 'definition'. The chemical applications of high frequency ultrasound are concerned essentially with measurements of either the velocity of sound through a medium or the degree to which the sound is absorbed as it passes through it. These applications will be discussed in more detail in. Such measurements are diagnostic in nature and do not effect the chemistry of the system under study.

When more powerful ultrasound at a lower frequency is applied to a system it is possible to produce chemical changes as a result of acoustically generated cavitation. Cavitation as a phenomenon was first identified and reported in 1895 by Sir John Thornycroft and Sidney Barnaby [5]. This discovery was the result of investigations into the inexplicably poor performance of a newly built destroyer HMS Daring. Her top speed was well below specifications and the problem was traced to the propeller blades that were incorrectly set and therefore not generating sufficient thrust. The rapid motion of

the blades through water was found to tear the water structure apart by virtue of simply mechanical action. The result of this was the production of what are now called cavitation bubbles. The solution to this problem lies in using very wide blades covering about two-thirds of the disc area of the propeller, so as to present a very large surface contact with the water. This helps to prevent disruption under the force necessary to propel the vessel. As ship speeds increased, however, this became a serious concern and the Royal Navy commissioned Lord Rayleigh to investigate. He produced a seminal work in the field of cavitation which confirmed that the effects were due to the enormous turbulence, heat, and pressure produced when cavitation bubbles imploded on or near to the propeller surface [6]. In the same work, he also observed that cavitation and bubble collapse was also the origin of the noise made when water is heated towards boiling point.

Since 1945 an increasing understanding of the phenomenon of cavitation has developed coupled with significant developments in electronic circuitry and transducer design (i.e. devices which convert electrical to mechanical signals and vice versa). As a result of this there has been a rapid expansion in the application of power ultrasound to chemical processes, a subject which has become known as "Sonochemistry".

1.2 THE POWER OF SOUND

Sound, as a general subject for study, is traditionally found in a physics syllabus but it is not a topic which is met in a chemistry course and so is somewhat unfamiliar to practising chemists. Sound is transmitted through a medium by inducing vibrational motion of the molecules through which it is travelling. This motion can be visualised as rather like the ripples produced when a pebble is dropped into a pool of still water. The waves move but the water molecules which constitute the wave revert to their normal positions after the wave has passed. An alternative representation is provided by the effect of a sudden twitch of the end of a horizontal stretched spring. Here the vibrational energy is transmitted through the spring as a compression wave which is seen to traverse its whole length. This is just a single compression wave and it does not equate to sound itself which is a whole series of such compression waves separated by rarefaction (stretching) waves in between. The pitch (or note) of the sound produced by this series of waves depends upon their frequency i.e. the number of waves which pass a fixed point in unit time. For middle C this is 256 per second. In physics sound waves are often shown as a series of vertical lines or shaded colour where line separation or colour depth represent intensity, or as a sine wave where intensity is shown by the amplitude (Figure 1.1).

SOUND MOTION IN A MEDIUM

Energy is transferred by molecular motion

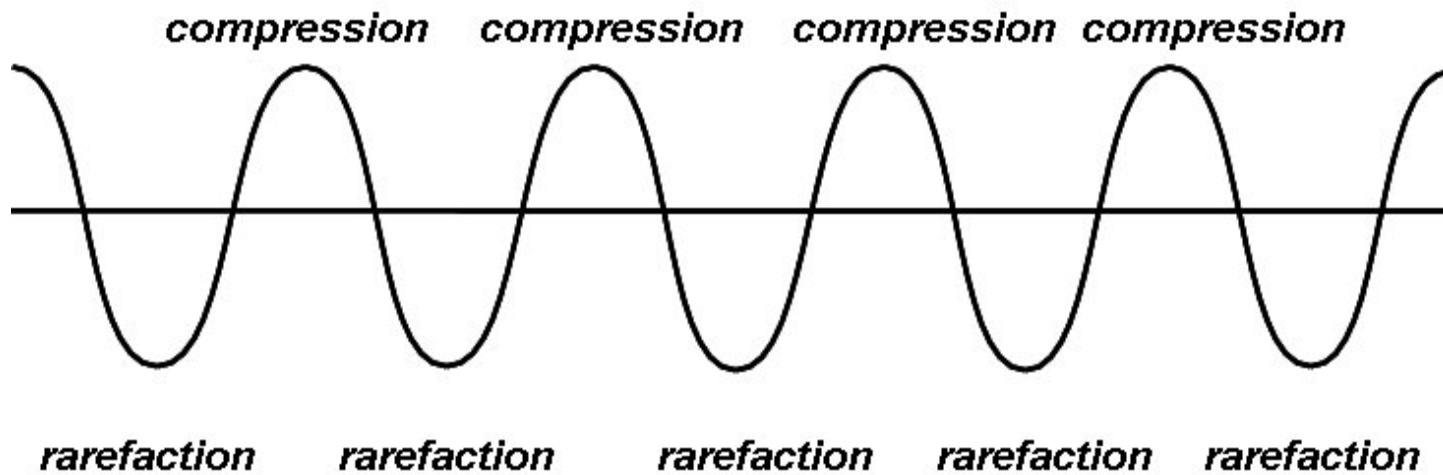
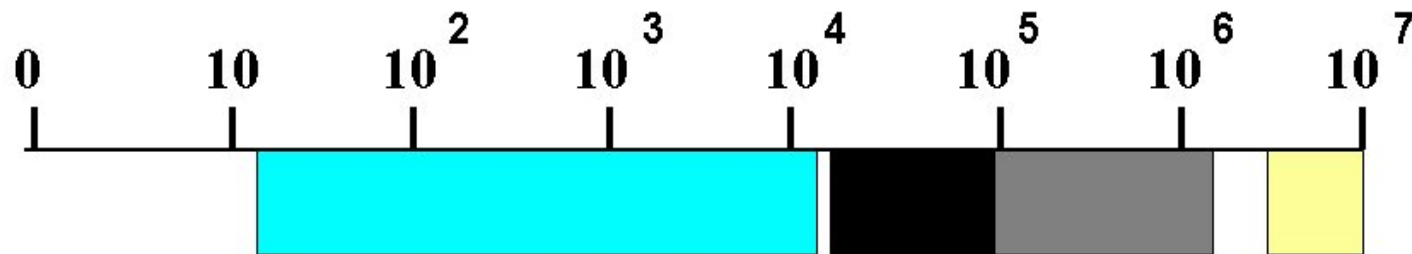


Figure 1.1: Sound transmission through a medium

The physical effects of sound vibrations are most easily experienced by standing in front of a loudspeaker playing music at high volume. The actual sound vibrations are transmitted through the air and are not only audible but can also be sensed by the body through the skin. The bass notes are felt through the body more easily than the high notes and this is connected with the frequency of the pressure pulse creating the sound. Low frequency sound becomes audible at around 18Hz (1Hz = 1 Hertz = 1 cycle per second) but as the frequency of the sound is raised (becoming more treble) it becomes more difficult for the body to respond and that sensation is lost. High frequency sound, while not noticeably effecting the body does cause severe annoyance to hearing e.g. feed back noise from a microphone through a loud speaker. At even higher frequencies the ear finds it difficult to respond and eventually the human hearing threshold is reached, normally around 18-20kHz for adults, sound beyond this limit is inaudible and is defined as ultrasound. The hearing threshold is not the same for other animal species thus dogs respond to ultrasonic whistles (so called "silent" dog whistles) and bats use frequencies well above 50kHz for navigation (Figure 1.2).

THE FREQUENCY RANGES OF SOUND



Human hearing



16Hz - 18kHz

Conventional power ultrasound



20kHz - 100kHz

Extended range for sonochemistry



20kHz - 2MHz

Diagnostic ultrasound



5MHz - 10MHz

Figure 1.2: Frequency ranges of sound

The broad classification of ultrasound as sound above 20kHz and up to 100MHz can be subdivided into two distinct regions Power and Diagnostic. The former is generally at lower frequency end where greater acoustic energy can be generated to induce cavitation in liquids, the origin of chemical effects. Sonochemistry normally uses frequencies between 20 and 40kHz simply because this is the range employed in common laboratory equipment. However since acoustic cavitation in liquids can be generated well above these frequencies, recent researches into sonochemistry use a much broader range (Figure 1.2). High frequency ultrasound from around 5MHz and above does not produce cavitation and this is the range used in medical imaging.

A whistle which generates a frequency 20kHz is inaudible to humans but perfectly audible to a dog - and produces no physical harm to either. It is however in the correct FREQUENCY range to affect chemical reactivity (Power Ultrasound). Yet such a whistle blown in a laboratory will not influence chemical reactions in any way. This is because the whistle is producing sound energy in air and airborne sound cannot be transferred into a liquid.

1.3 REFERENCES

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3. J.Curie and P.Curie, Compt. Rend. (1881) **93**, 1137.
4. F.Galton, Inquiries into human faculty and development (1883) MacMillan, London.
5. J.Thornycroft and S.W.Barnaby, "Torpedo boat destroyers", Proc.Inst.Civil.Engineers (1895) **122**, 51

2. ACOUSTIC CAVITATION

Power ultrasound enhances chemical and physical changes in a liquid medium through the generation and subsequent destruction of cavitation bubbles. Like any sound wave ultrasound is propagated via a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. At sufficiently high power the rarefaction cycle may exceed the attractive forces of the molecules of the liquid and cavitation bubbles will form. Such bubbles grow by a process known as rectified diffusion i.e. small amounts of vapour (or gas) from the medium enters the bubble during its expansion phase and is not fully expelled during compression. The bubbles grow over the period of a few cycles to an equilibrium size for the particular frequency applied. It is the fate of these bubbles when they collapse in succeeding compression cycles which generates the energy for chemical and mechanical effects (Figure 2.1). Cavitation bubble collapse is a remarkable phenomenon induced throughout the liquid by the power of sound. In aqueous systems at

an ultrasonic frequency of 20kHz each cavitation bubble collapse acts as a localised "hotspot" generating temperatures of about 4,000 K and pressures in excess of 1000 atmospheres [1-3].

ACOUSTIC CAVITATION

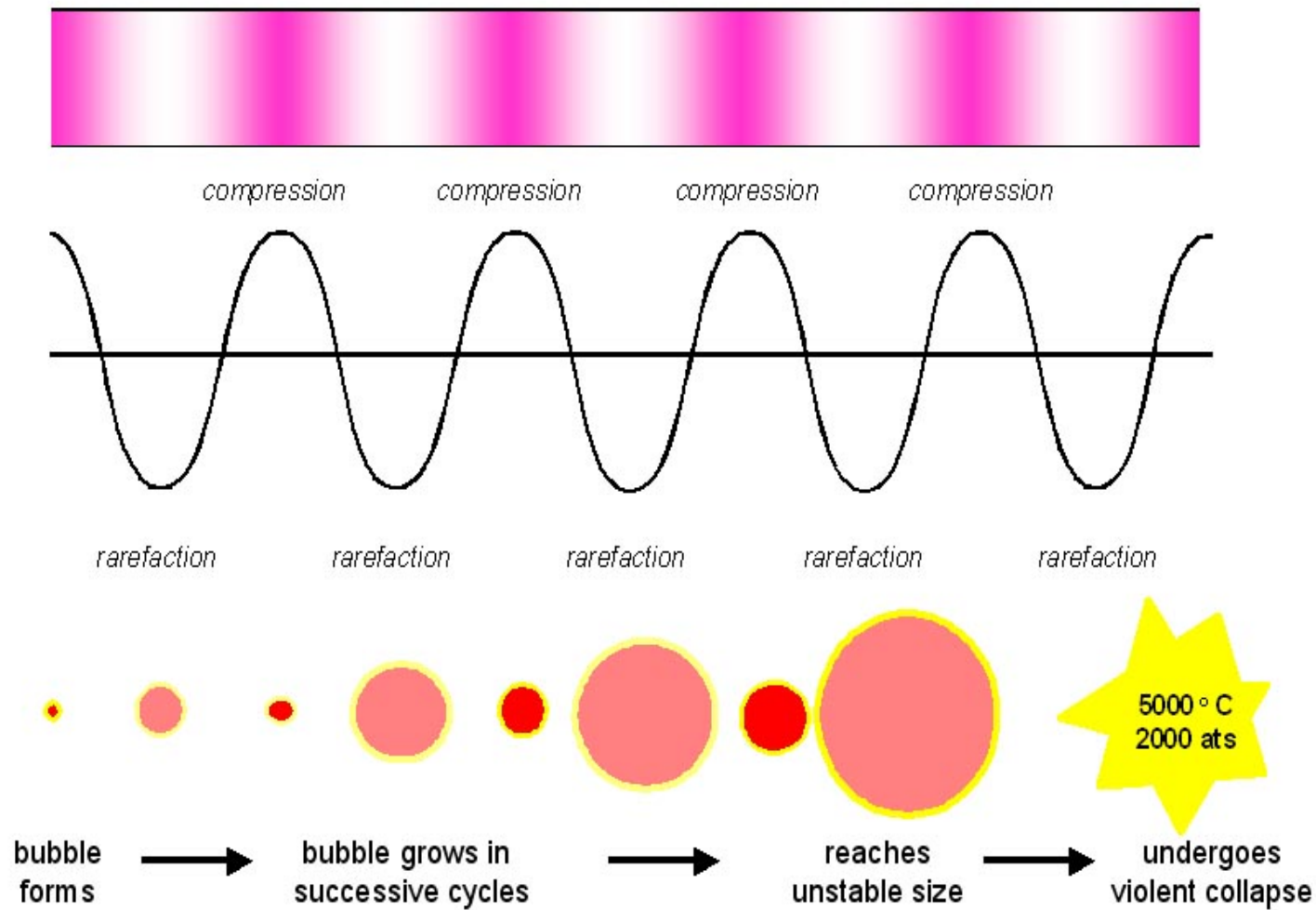


Figure 2.1: Generation of an acoustic bubble

The cavitation bubble has a variety of effects within the liquid medium depending upon the type of system in which it is generated. These systems can be broadly divided into homogeneous liquid, heterogeneous solid/liquid and heterogeneous liquid/liquid. Within chemical systems these three groupings represent most processing situations.

2.1 HOMOGENEOUS LIQUID-PHASE REACTIONS

- (i) in the bulk liquid immediately surrounding the bubble where the rapid collapse of the bubble generates shear forces which can produce mechanical effects and
- (ii) in the bubble itself where any species introduced during its formation will be subjected to extreme conditions of temperature and pressure on collapse leading to chemical effects. (Figure 2.2).

ACOUSTIC CAVITATION

in a homogeneous liquid medium

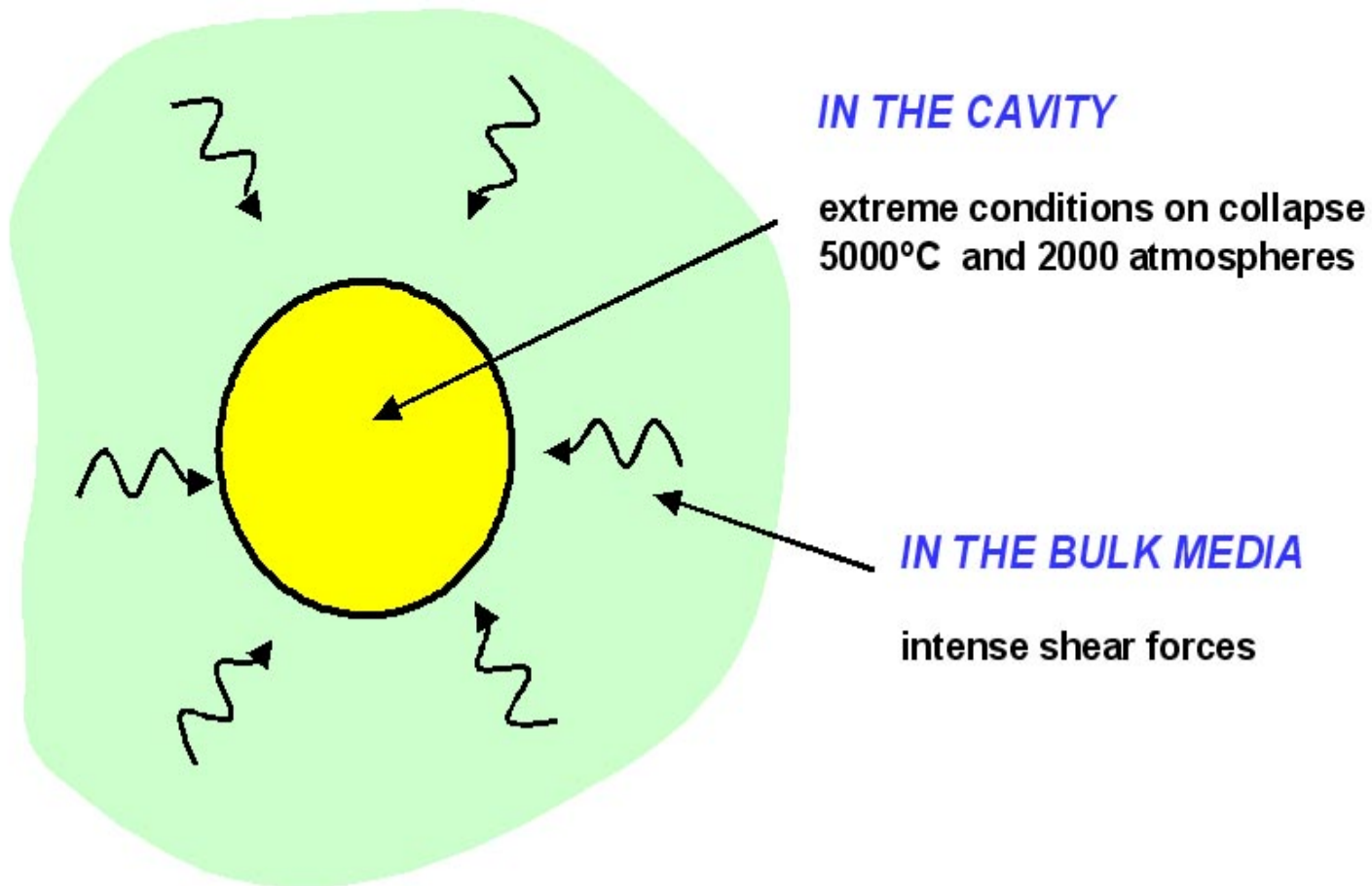


Figure 2.2: Acoustic cavitation in a homogeneous liquid

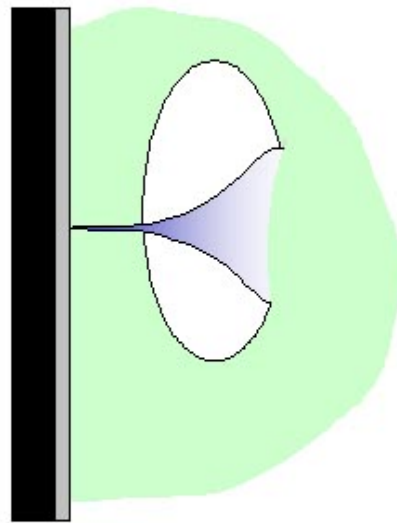
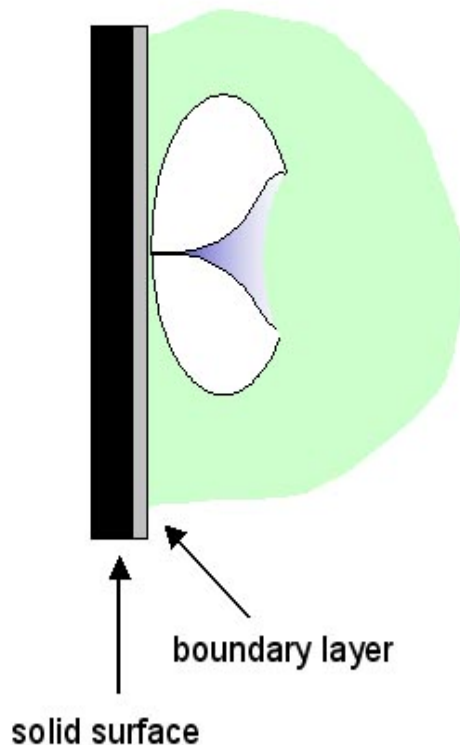
2.2 CAVITATION NEAR A SURFACE

Unlike cavitation bubble collapse in the bulk liquid, collapse of a cavitation bubble on or near to a surface is unsymmetrical because the surface provides resistance to liquid flow from that side. The result is an inrush of liquid predominantly from the side of the bubble remote from the surface resulting in a powerful liquid jet being formed, targeted at the surface (Figure 2.3). The effect is equivalent to high pressure jetting and is the reason that ultrasound is used for cleaning. This effect can also activate solid catalysts and increase mass and heat transfer to the surface by disruption of the interfacial boundary layers.

ACOUSTIC CAVITATION

Collapse at or near a solid surface

Inrush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surface



Surface cleaning
destruction of boundary layer
surface activation
improved mass and heat transfer

Figure 2.3: Cavitation bubble collapse at or near a solid surface

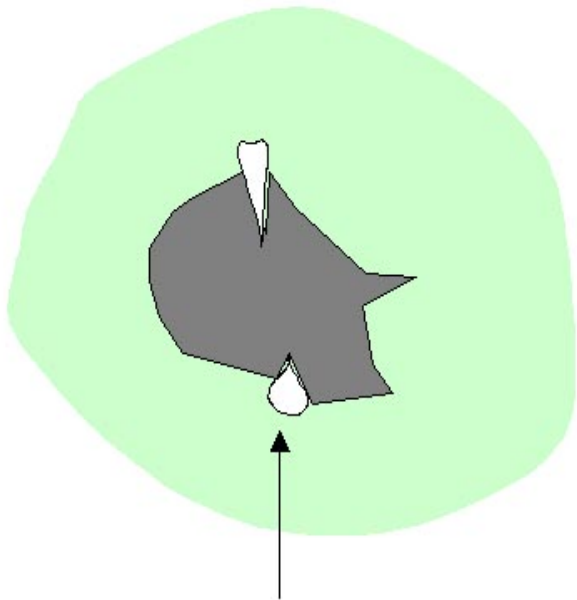
2.3 HETEROGENEOUS POWDER-LIQUID REACTIONS

Acoustic cavitation can produce dramatic effects on powders suspended in a liquid (Figure 2.4). Surface imperfections or trapped gas can act as the nuclei for cavitation bubble formation on the surface of a particle and subsequent surface collapse can then lead to shock waves which break the particle apart. Cavitation bubble collapse in the liquid phase near to a particle can force it into rapid motion. Under these circumstances the general dispersive effect is accompanied by interparticle collisions which can lead to erosion, surface cleaning and wetting of the particles and particle size reduction.

ACOUSTIC CAVITATION

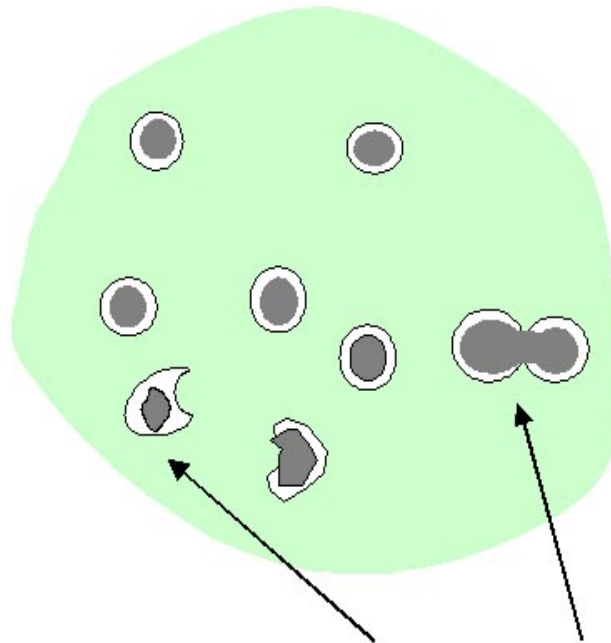
In the presence of a suspended powder

LARGE PARTICLES



surface cavitation due to defects
leading to **fragmentation**

SMALL PARTICLES



collision can lead to
SURFACE EROSION or FUSION

Figure 2.4: Acoustic cavitation in a liquid with a suspended powder

In heterogeneous liquid/liquid reactions, cavitation collapse at or near the interface will cause disruption and mixing, resulting in the formation of very fine emulsions (Figure 2.5).

ACOUSTIC CAVITATION

Heterogeneous liquid / liquid system

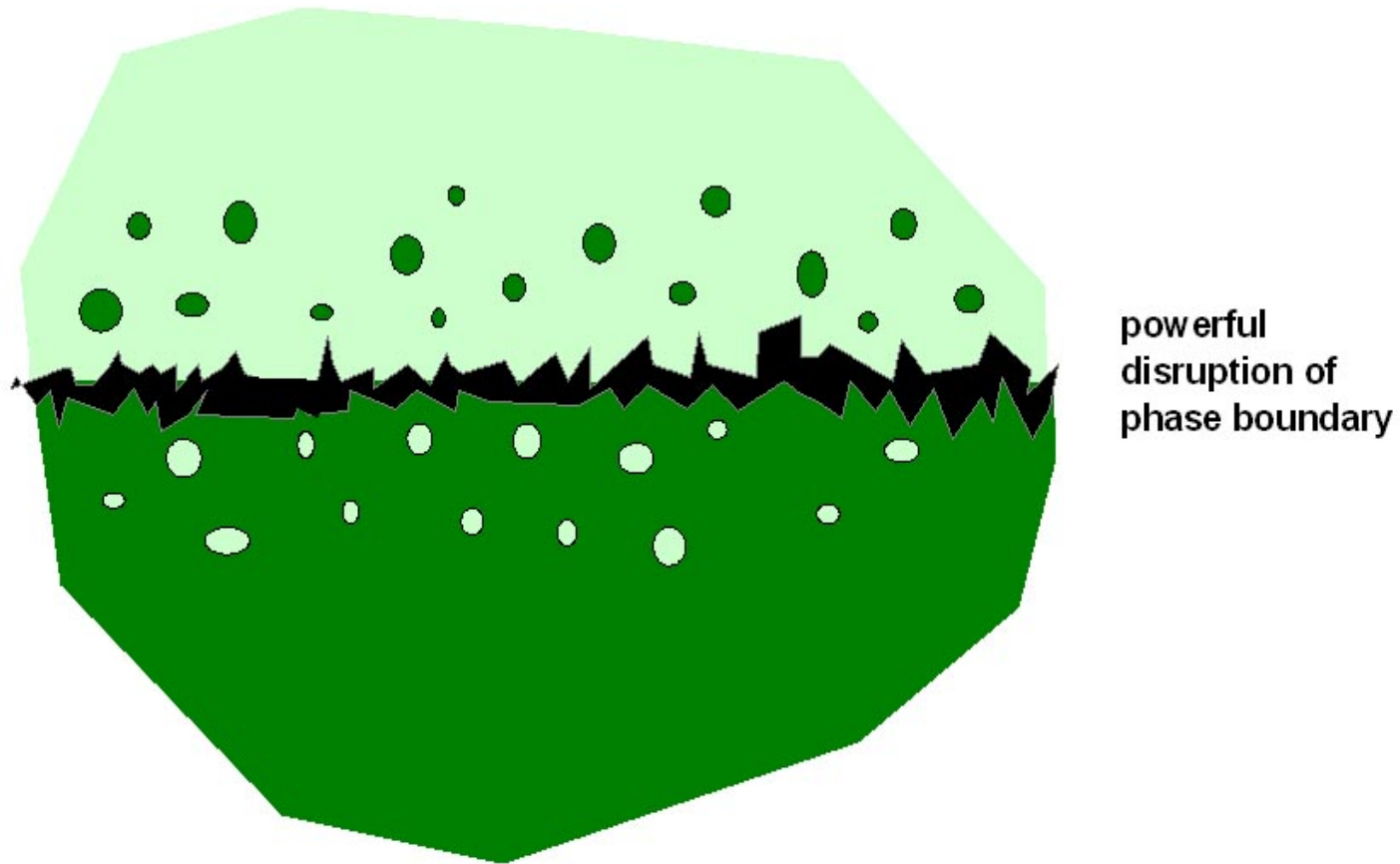


Figure 2.5: Cavitation effects in a heterogeneous liquid/liquid system

2.4 REFERENCES FOR CAVITATION

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2. A.Henglein, Ultrasonics (1987) **25**, 6.
3. K.S.Suslick, Science (1990) **247**, 1439.

3. TRANSDUCERS

A transducer is the name for a device capable of converting one form of energy into another, a simple example being a loudspeaker which converts electrical energy to sound energy. Ultrasonic transducers are designed to convert either mechanical or electrical energy into high frequency sound and there are three main types: gas driven, liquid driven and electromechanical.

3.1 GAS-DRIVEN TRANSDUCERS

These are, quite simply, whistles with high frequency output (the dog whistle is a familiar example). The history of the generation of ultrasound via whistles dates back 100 years to the work of F.Galton who was interested in establishing the threshold levels of human hearing. He produced a whistle that generated sound of known frequencies and was able to determine that the normal limit of human hearing is around 18kHz. Galton's whistle was constructed from a brass tube with an internal diameter of about two millimetres (Figure 3.1) and operated by passing a jet of gas through an orifice into a resonating cavity. On moving the plunger the size of the cavity could be changed to alter the "pitch" or frequency of the sound emitted. An adaptation of this early principle is to be found in some dog whistles that have adjustable pitch.

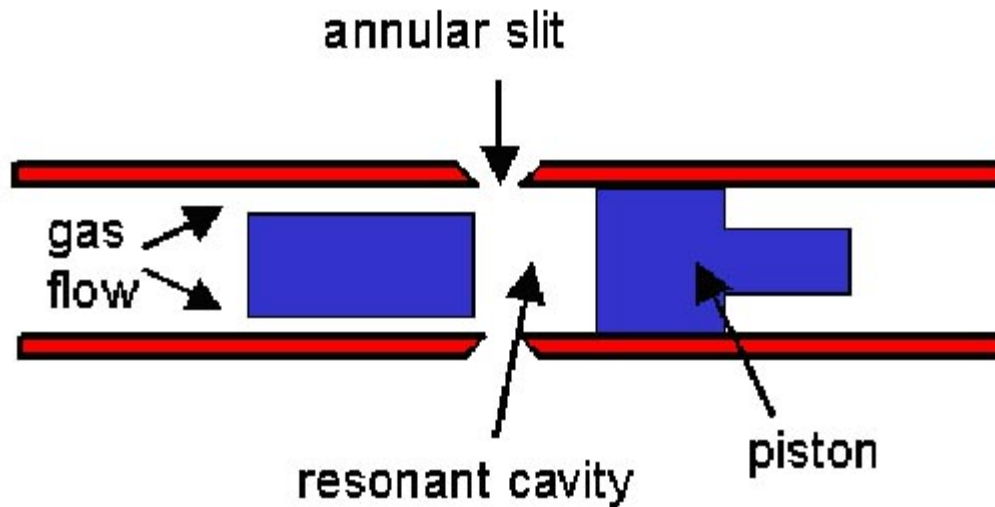


Figure 3.1: Galton Whistle

An alternative form of gas generated ultrasound is the siren. When a solid object is passed rapidly back-and-forth across a jet of high pressure gas it interferes with the gas flow and produces sound of the same frequency at which the flow is disturbed. A siren can be designed by arranging that the nozzle of a gas jet impinges on the inner surface of a cylinder through which there are a series of regularly spaced perforations. When the cylinder is rotated the jet of gas emerging from the nozzle will rapidly alternate between facing a hole or the solid surface. The pitch of the sound generated by this device will depend upon the speed of rotation of the cylinder. Neither type of transducer has any significant chemical application since the efficient transfer of acoustic energy from a gas to a liquid is not possible. However whistles are used for the atomization of liquids.

The conventional method of producing an atomized spray from a liquid is to force it at high velocity through a small aperture. (A typical domestic examples being a spray mist bottle for perfume). The disadvantage in the design of conventional equipment is that the requirement for a high liquid velocity and a small orifice restricts its usage to low viscosity liquids and these atomizers are often subject to blockage at the orifice.

Figure 3.2 shows a schematic gas driven atomizer. The system comprises of an air or gas jet, which is forced into an orifice where it expands and produces a shock wave. The result is an intense field of sonic energy focused between the nozzle body and the resonator gap. When liquid is introduced into this region it is vigorously sheared into droplets by the acoustic field. Air by-passing the resonator carries the atomized droplets downstream in a fine soft plume shaped spray. The droplets produced are small and have a low forward velocity. Atomized water sprays have many uses including dust suppression in industry and humidifiers for horticultural use under glass.

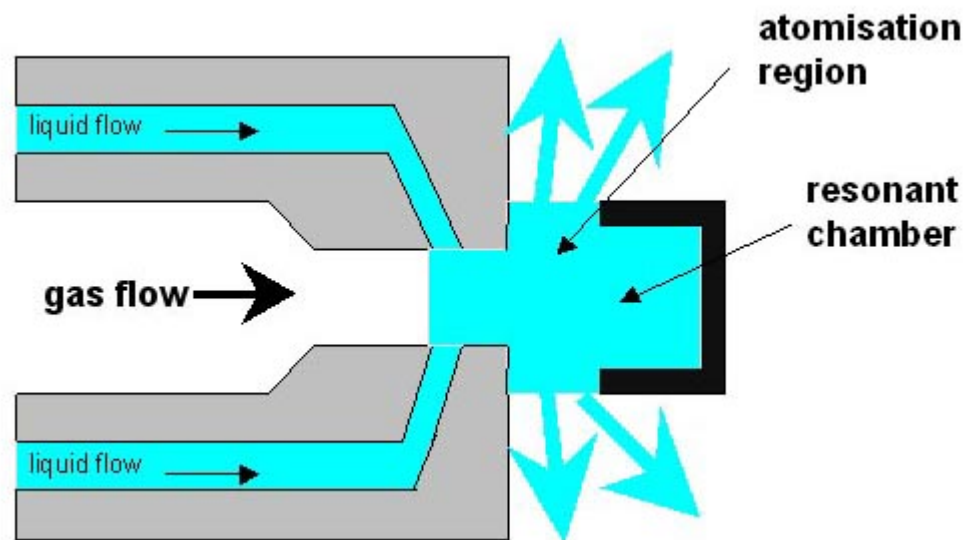


Figure 3.2: Gas Driven Atomizer

3.2 LIQUID-DRIVEN TRANSDUCERS

In essence this type of transducer is a "liquid whistle" and generates cavitation via the motion of a liquid rather than a gas. Process material is forced at high velocity by the homogeniser pump through a special orifice from which it emerges as a

jet which impacts upon a steel blade (Figure 3.3). There are two ways in which cavitation mixing can occur at this point. Firstly through the Venturi effect as the liquid rapidly expands into a larger volume on exiting the orifice and secondly via the blade which is caused to vibrate by the process material flowing over it. The relationship between orifice and blade is critically controlled to optimise blade activity. The required operating pressure and throughput is determined by the use of different sizes and shapes of the orifices and the velocity can be changed to achieve the necessary particle size or degree of dispersion. With no moving parts, other than a pump, the system is rugged and durable. When a mixture of immiscible liquids is forced through the orifice and across the blade cavitation mixing produces extremely efficient homogenization.

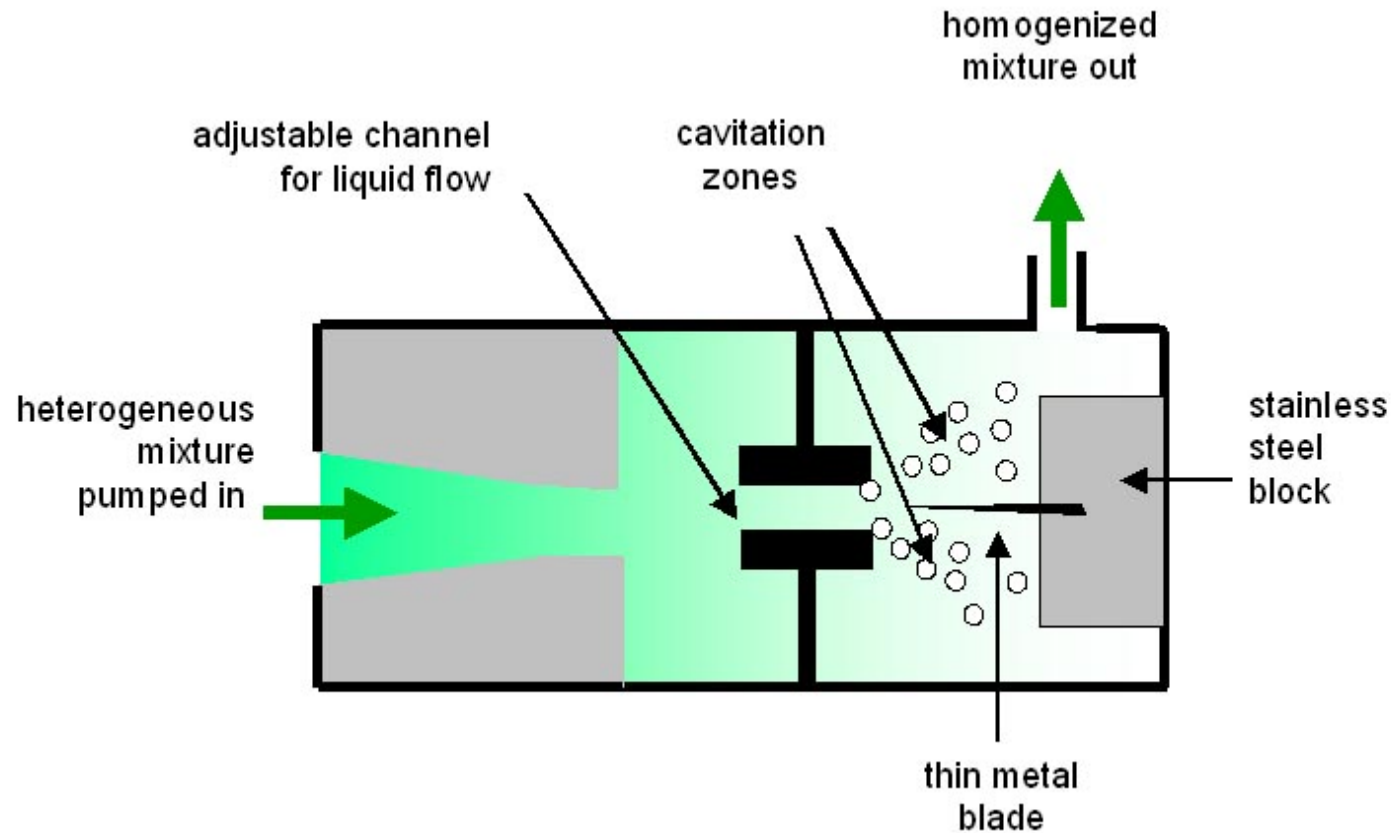


Figure 3.3: Liquid Whistle

3.3 ELECTROMECHANICAL TRANSDUCERS

The two main types of electromechanical transducers are based on either the piezoelectric or the magnetostrictive effect. The most commonly used of which are piezoelectric transducers, generally employed to power the bath and probe type sonicator systems. Although more expensive than mechanical transducers, electromechanical transducers are by far the most versatile.

3.3.1 Magnetostrictive Transducers

Historically magnetostrictive transducers were the first to be used on an industrial scale to generate high power ultrasound. These are devices which use an effect found in some materials e.g. nickel which reduce in size when placed in a magnetic field and return to normal dimensions when the field is removed (magnetostriction). When the magnetic field is applied as a series of short pulses to a magnetostrictive material it vibrates at the same frequency. In simple terms such a transducer can be thought of as a solenoid in which the magnetostrictive material (normally a laminated metal or alloy) forms the core with copper wire winding. To avoid magnetic losses two such solenoids are wound and connected in a loop (Figure 3.4).

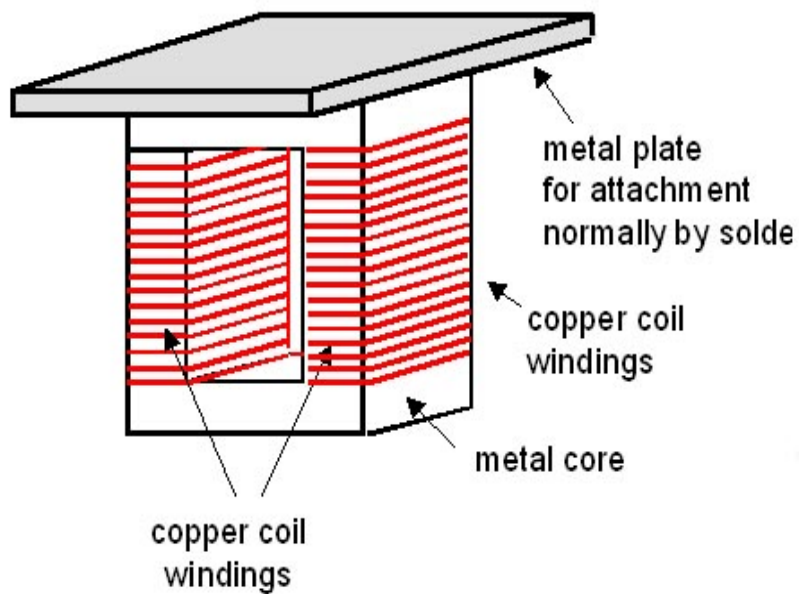


photo courtesy of Lewis Corporation, USA

Figure 3.4: Piezoelectric Sandwich Transducer

The major advantages of magnetostrictive systems are that they are of an extremely robust and durable construction and provide very large driving forces. This makes them an attractive proposition for heavy duty industrial processing. There are however two disadvantages, firstly the upper limit to the frequency range is 100kHz, beyond which the metal cannot respond fast enough to the magnetostrictive effect, and secondly the electrical efficiency is less than 60% with significant losses emerging as heat. As a result of the second of these problems all magnetostrictive transducers subject to extended use are liquid cooled. This has meant that piezoelectric transducers (see below) which are more efficient and operate over a wider frequency range are generally considered to be the better choice in sonochemistry, especially in laboratory situations. However now that a range of industrial applications for sonochemistry are under consideration, particularly those requiring heavy duty continuous usage at high operating temperatures, the magnetostrictive transducer is coming back into consideration.

Many improvements in the operating efficiency of this type of transducer have been made all of which are based on finding a more efficient magnetostrictive core. The original nickel based alloys have been replaced by more electrically efficient cobalt/iron combinations and, more recently, aluminium/iron with a small amount of chromium. One of the latest developments in magnetostrictive technology has been the introduction of a new material called TERFINOL-D. This is an alloy of the rare earths terbium and dysprosium with iron which is zone refined to produce a material almost in the form of a single crystal. It can be produced in various forms, rods, laminates, tubes etc and has several major advantages over the more conventional alloys used. A magnetostrictive transducer based on this material can generate more power than a conventional piezoelectric transducer, it is compact (about 50% smaller) and lighter than other magnetostrictives. It does have the same problem as other such devices in that it has an upper limit of frequency response - in this case 70kHz.

3.3.2 Piezoelectric Transducers

The most common types of transducer used for both the generation and detection of ultrasound employ materials that exhibit the piezoelectric effect, discovered over a century ago. Such materials have the following two complementary properties:

1. The direct effect - when pressure is applied across the large surfaces of the section a charge is generated on each face equal in size but of opposite sign. This polarity is reversed if tension is applied across the surfaces.
2. The inverse effect - if a charge is applied to one face of the section and an equal but opposite charge to the other face then the whole section of crystal will either expand or contract depending on the polarity of the applied charges. Thus on applying

rapidly reversing charges to a piezoelectric material fluctuations in dimensions will be produced. This effect can be harnessed to transmit ultrasonic vibrations from the crystal section through whatever medium with which it is in contact.

Quartz was the piezoelectric material originally used in devices such as the very early types of ASDIC underwater ranging equipment. Quartz is not a particularly good material for this purpose because of its mechanical properties, it is a somewhat fragile and difficult to machine. Modern transducers are based on ceramics containing piezoelectric materials. These materials cannot be obtained as large single crystals and so, instead, they are ground with binders and sintered under pressure at above 1000°C to form a ceramic. Cooling from above their ferroelectric transition temperature in a magnetic field then aligns the crystallites of the ceramic. Such transducers can be produced in different shapes and sizes. Nowadays the most frequently employed piezoceramic contains lead zirconate titanate (commonly referred to as PZT where the P represents plumbum - the chemical term for the element lead - and the Z and T are initials from the name of the salts). The most common form is a disk with a central hole. In a power transducer it is normal practice to clamp two of these piezoelectric disks between metal blocks which serve both to protect the delicate crystalline material and to prevent it from overheating by acting as a heat sink. The resulting "sandwich" provides a durable unit with doubled mechanical effect (Figure 3.5). The unit is generally one half wavelength long (although multiples of this can be used). The peak to peak amplitudes generated by such systems are normally of the order of 10-20 microns and they are electrically efficient. Generally piezoelectric devices must be cooled if they are to be used for long periods at high temperatures because the ceramic material will degrade under these conditions.

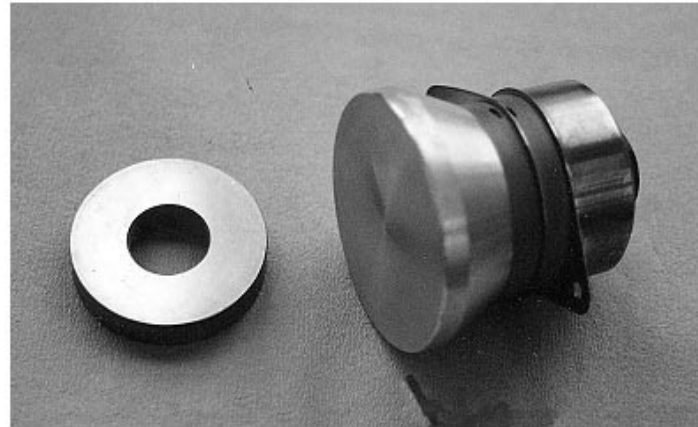
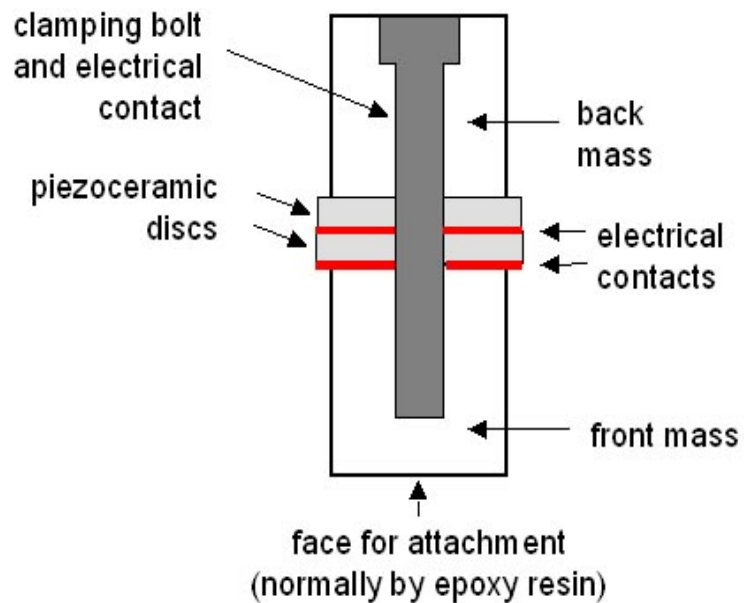


photo courtesy of Langford Ultrasonics, UK

Figure 3.5: Piezo electric Transducer

Such transducers are highly efficient (>95%) and, depending on dimensions, can be used over the whole range of ultrasonic frequencies from 20kHz to many MHz. They are the exclusive choice in medical scanning which uses frequencies above 5MHz.

3.3.3 Low frequency vibrating bar transducer system

A significantly different system has been introduced to large scale processing and this involves audible frequency vibrations generated in a large cylindrical steel bar⁶. The bar is driven into a clover leaf type of motion by firing three powerful magnets in sequence which are located at each end of the bar. The bar is supported by air springs so that the ends and the centre are then caused to rotate at a resonance frequency depending on its size (Figure 3.6). One such unit, operating at a power of 75kW, drives a bar which is 4.1 metre long and 34 cm in diameter at its resonance frequency of 100Hz. The bar itself weighs 3 tonnes and produces a vibrational amplitude at each end of 6mm considerably larger than

the amplitudes available through sonochemical processing and hence better for the dispersal of materials in liquids. This type of system can be used in chemical processing applications by fixing a robust cylindrical steel cell to each end of the bar. Material in the form of a liquid or slurry can then be pumped through the cells in order to perform operations such as mixing, grinding and the destruction of hazardous waste. Hard spherical grinding balls are often added to the cells to assist in these processes. The combination of the large vibrational energy together with the motion of grinding balls appears to provide an extremely good alternative to conventional mixers and grinders. Other units using smaller sized bars operating at higher, though still audible, frequencies have also been built.

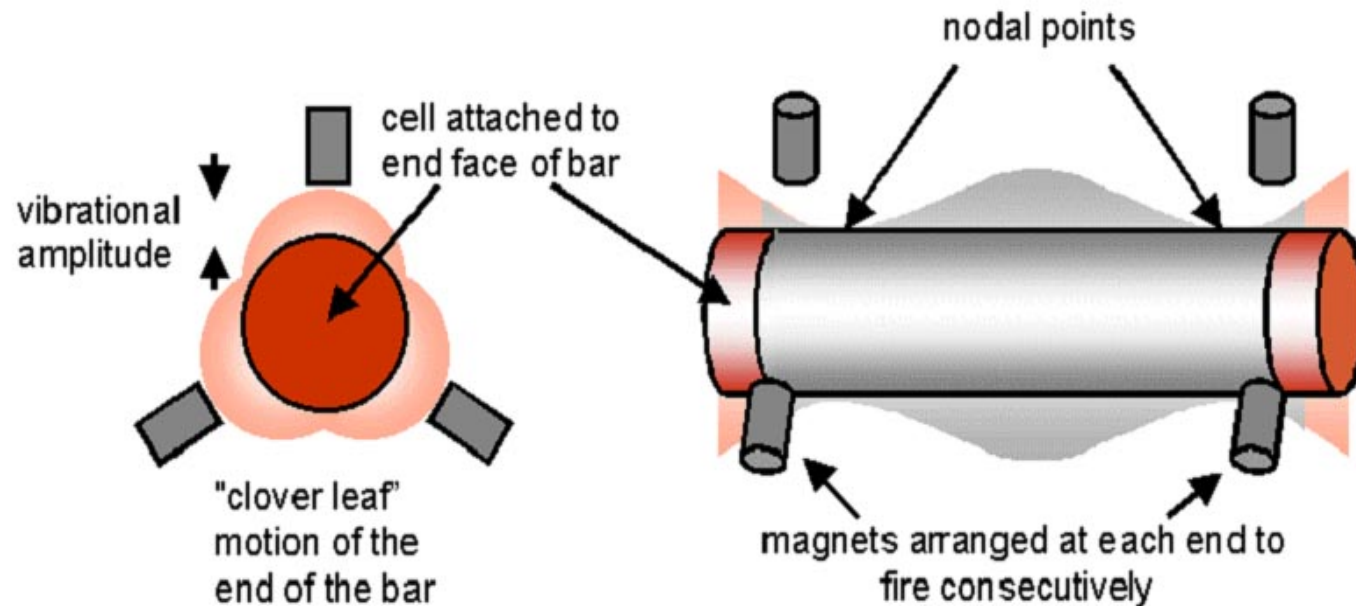


Figure 3.6: Vibrating Bar Transducer

4. REACTOR DESIGN AND SCALE UP

The design of sonochemical reactors and the rationale for the scale up of successful laboratory ultrasonic experiments are clear goals in sonochemistry and sonoprocessing. Indeed the progress of sonochemistry in green and sustainable chemistry is dependent upon the possibility of scaling up the excellent laboratory results for industrial use. The first step in the progression of a sonochemical process from laboratory to large scale is to determine whether the ultrasonic enhancement is the result of a mechanical or a truly chemical effect. If it is mechanical then ultrasonic pre-treatment of slurry may be all that is required before the reacting system is subjected to a subsequent conventional type reaction. If the effect is truly sonochemical however then sonication must be provided during the reaction itself. The second decision to be made is whether the reactor should be of the batch or flow type. Whichever type is to be used there are only three basic ways in which ultrasonic energy can be introduced to the reacting medium.

- Immerse reactor in a tank of sonicated liquid (*e.g. flask dipped into a cleaning bath*)
- Immerse an ultrasonic source directly into the reaction medium (*e.g. probe placed in a reaction vessel*)
- Use reactor constructed with vibrating walls (*e.g. a tube operating through radial vibrations*)

4.1 Batch Treatment

The obvious batch treatment processor is the ultrasonic cleaning bath which is a readily available source of low intensity ultrasonic irradiation generally at a frequency of around 40kHz. A reactor based on this design might require adaptation to provide chemically resistant walls, a sealed lid for work under an inert atmosphere and mechanical stirring. Using this system for large volume treatment the acoustic energy entering the reaction would be quite small and any stirrer and fittings in the bath would cause attenuation of the sound energy.

An alternative configuration would involve using a submersible transducer assembly which have been used for many years in the cleaning industry. It consists of a sealed unit within which transducers are bonded to the inside of one face and can be designed to fit into any existing reaction vessel.

4.2 Flow Systems

Flow Systems are generally regarded as the best approach to industrial scale sonochemistry. The general arrangement would consist of a flow loop outside a normal batch reactor which acts as a reservoir within which conventional chemistry can occur. Such an arrangement allows the ultrasonic dose of energy entering the reaction to be controlled by transducer power input and flow rate (residence time). Temperature control is achieved through heat exchange in the circulating reaction mixture.

Pipes of various cross-sectional geometry can be converted to flow processors by generating ultrasonic vibrations through their walls. The length of pipe must be accurately designed so that a null point exists at each end and it can then be retro-fitted to existing pipework. Such systems are capable of handling high flow rates and viscous materials. There are four common cross-sectional geometries: rectangular, pentagonal, hexagonal and circular. The pentagonal pipe provides a fairly uniform ultrasonic field since the energy from each irradiating face is reflected at an angle from the two opposite faces. The other configurations provide a "focus" of energy in the centre where direct energy and that reflected from the opposite wall meet.

4.3 References

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- 4 *A novel angular geometry for the sonochemical silver recovery process at cylinder electrodes*, B.G. Pollet, J.P. Lorimer, S.S. Phull, T.J. Mason and J.-Y. Hihn, Ultrasonics Sonochemistry **10**, pp 217-222 (2003).

5. EXAMPLES OF RESEARCH PROJECTS

“Prospects for scale-up in the ultrasonic extraction of natural materials”

“Large scale sonochemical processing”

“Ultrasonic intensification of chemical processing and related operations”

“Sonic and ultrasonic removal of chemical contaminants from soil in the laboratory and on a large scale”

[Return to top](#)