

ULTRASONIC MONITORING OF PARTICULATE SUSPENSIONS IN-PROCESS: PHYSICS, TECHNOLOGY AND APPLICATIONS

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Abstract: Ultrasonic compression wave propagation is sensitive to the physical state of particulate liquid suspensions – colloids and emulsions. It is possible to estimate dispersed particle size distribution (PSD) from measurements of wave attenuation and/or phase velocity as functions of frequency. It is also possible to detect and characterise dynamic phenomena such as flocculation, network formation and crystallisation. Despite these possibilities the take-up of ultrasonic techniques has been slow, even though the methods have considerable advantages over competing techniques such as laser light scattering in that they can be applied to optically opaque liquids contained in opaque metal vessels and pipe work. In this paper we discuss the physical principles underlying the ultrasonic characterisation of particulate mixtures covering both hydrodynamic and scattering theories, and showing how PSDs are obtained from wave propagation data. On the basis of these theories combined with experimental results from real materials we review the ultrasonic signal conditions that are required for the successful characterisation of suspensions, particularly in relation to the performance of the electronic system. We show how the available signal bandwidth determines the complexity of the information that can be gained about the test material. We conclude with examples of ultrasonic systems that we have built for both laboratory bench top use and for application in-line to pipe work on process plant.

Introduction: Ultrasonic compression wave attenuation and phase velocity exhibit a frequency dependence that depends on the physical properties of the material through which the wave propagates. In the case of particulate mixtures they depend on the physico-thermal properties of both phases and on the dispersed phase particle size distribution (PSD). Changes in the state of the mixture due to, for example, flocculation or crystallisation can be recognised and quantified from measurements of the ultrasonic attenuation spectra [1,2]. Most ultrasonic systems for such measurements are custom assembled from commercial components and do not lend themselves to in-process applications. A few quite sophisticated commercial instruments are available, such as the *Ultrasizer* (Malvern Instruments Ltd, UK), but again these are not primarily designed for process use. Ultrasound is highly suited to process applications because it can be used to probe optically opaque materials through the opaque walls of process pipe-work and vessels. In this paper we outline the underlying physics of the interactions between ultrasonic waves and particulate mixtures, showing how measured ultrasonic propagation variables are sensitive to PSD. We next consider how the signal to noise performance of the electronic-ultrasonic system, combined with the dynamic range of measured attenuation data, sets limits on the available measurement bandwidth and ultimately the amount of information which can be gained in a measurement on any given colloidal mixture. The ideas are then considered in the context of the constraints on the sizes of pipes and vessels on which measurements are to be made, leading to a simple procedure for the assessment of the feasibility of any given measurement.

Physics of ultrasonic wave propagation in particulate mixtures: In a homogeneous liquid mixture ultrasonic compression wave propagation can be represented by the following expression:

$$A(\omega, x) = A(\omega, 0) e^{-\alpha(\omega)x} e^{\frac{i\omega x}{c(\omega)}} \quad (1)$$

In this expression x is the distance the wave has travelled, ω is angular frequency, and i the complex operator $(-1)^{1/2}$. $A(0,\omega)$ is the spectral amplitude of the wave at the origin, $x=0$, and $A(x,\omega)$ the amplitude after propagation through a distance x . $\alpha(\omega)$ is the frequency dependent attenuation coefficient expressed in Nepers (Np) per metre. $c(\omega)$ is the phase velocity of the wave and will always show a small frequency dependence where attenuation is non zero. In water with no suspended particles phase velocity variation with frequency is negligible and the attenuation generally can be neglected in comparison with likely attenuations when suspended particles are present. In oily liquids both attenuation and phase velocity can be strong functions of frequency due to the effects of viscosity and/or molecular scale relaxations in the liquid continuum. In all cases ultrasonic wave interactions with the suspended particles lead to changes in $\alpha(\omega)$ and $c(\omega)$ which are measurable and form the basis for the estimation of PSD. Where the density of the particles is more than twice that of the continuous phase the dominating phenomena are hydrodynamic and losses arise from the to-fro motions of the particles with respect to the continuous phase, driven by pressure gradient oscillations in the ultrasonic field. Where the densities of the two phases are of similar order (eg oil in water emulsions, polymer colloids) hydrodynamic effects are less important and losses become dominated by elastic and thermal effects which cause the particle to undergo a breathing motion with respect to the surrounding fluid at the same time as mode conversion of wave energy to heat, all of which affect $\alpha(\omega)$ and $c(\omega)$ in a measurable way. There are a great number of mathematical formulations which incorporate some or all of the phenomena just outlined. A workable hydrodynamic theory can be found in Harker and Temple [3] and an extension to include thermal effects is available in a more recent work (Evans and Attenborough [4]). The theory which has found most use in many laboratories world wide is attributable to Epstein and Carhart [5] and Allegra and Hawley [6], generally known as the ECAH theory and reviewed in some detail by Challis *et al* [7]. Its advantage is that it incorporates all of the physical effects cited above and is thus applicable across a broad range of mixtures. However, it suffers a number of disadvantages. The most significant of these is that it is computationally intensive and prone to problems of ill-conditioning in matrix operations (see O'Neill *et al* [8]) although a number of commercial codes are becoming available. There is also a requirement for quantitative knowledge of 14 physical constants, seven for each phase, to represent the mixture. The theory is not self-consistent in that a non physical result is obtained if the fractional volume occupied by the dispersed phase is set to 100%; indeed, the accuracy of the theory can diminish rapidly when dispersed phase volume fractions rise above around 30% for liquid droplet particles and around 10% for solid particles. The theory also assumes that the particles are spherical, although this is not always limiting because the ultrasonic wavelengths involved in a typical ultrasonic system generally greatly exceed particle size. In its simplest form the theory gives

$$\frac{\omega}{c(\omega)} + i\alpha(\omega) = k_c \left[1 + \frac{3\phi}{ik_c^3 R^3} (A_o + 3A_1 + 5A_2) \right]^{1/2} \quad (2)$$

Here the left-hand side pertains to the whole mixture. k_c is the equivalent expression (ie the complex wave number) for the continuous phase. R is the dispersed particle radius and ϕ the dispersed phase volume fraction. A_n are partial wave coefficients which depend on the particle size and the physico-thermal properties of both phases. A_1 incorporates visco-inertial effects (the to-fro particle motion) and A_o includes all of the other physical phenomena cited above. A_2 is the first of a series of higher order terms (A_3 A_4 etc) which are dominated by particle resonances which, in most colloidal materials, occur at very high frequencies (>100MHz) which are presently out of the range of measurement for process applications. For polydisperse mixtures the right hand side of equation 2 is modified to sum over a range of particle sizes, and corresponding volume fractions and coefficients A_n . On the basis of this theory the basic process of colloid particle sizing begins with a measurement of $\alpha(\omega)$ as a function of frequency – the ultrasonic

attenuation spectrum. The model of equation 2 is run on a computer adapting on candidate distributions of ϕ and R until a match to measured attenuation is reached in a least mean squared error sense. The adapted distribution of ϕ and R is then taken as the measured PSD. In many cases equation 2 or its polydisperse form can be simplified; for an oil droplet in water emulsion it is frequently possible to exclude partial wave coefficients of order greater than zero. For suspensions in which the particles have a relative density greater than around 2 one can consider only the coefficient A_1 . This is essentially the case in which the wave attenuation results from hydrodynamic phenomena and it may therefore be possible to employ alternatives to the ECAH theory such as the hydrodynamic formulation to the ultrasonic wave number of Harker and Temple [3] which can be expressed in the general form

$$k^2 = \omega^2 \rho^* \beta^* \frac{A - i(\gamma / \omega)}{B - i(\gamma / \omega)} \quad (3)$$

Here ρ^* and β^* are the volume averaged density and compressibility of the mixture and A and B are functions of the densities of the two phases. γ is a drag function which in its simplest form is

$$\gamma = 6\pi R \eta \quad (4)$$

where η is viscosity. As far as the current authors are aware the theory has not yet been modified to take account of many different particle sizes in suspension although we believe that this is possible. A significant advantage of the theory is that the drag/viscosity term can be modified to take account of the effects of neighbouring particles, see Strout [9], and also other physical phenomena such as *induced mass* which can be expressed as an imaginary part in the viscosity. Work on these possibilities is ongoing with the aim of adapting the model on PSD to fit measured attenuation data in the same manner as is currently done in the context of the ECAH theory.

Hardware systems and the effects of noise: The most likely configuration of ultrasonic and electronic hardware is shown in figure 1. Ultrasonic transducers for transmit (Tx) and receive (Rx) functions are placed on either side of a test cell integrated into process pipe-work. The transmitted signal passes through the test medium, is received by Rx, amplified, and then digitised for subsequent processing to calculate $\alpha(\omega)$ and $c(\omega)$. The data which are output from the digitiser will be distorted by unavoidable electronic noise which sets limits on the range of attenuation that is measurable. Ultrasonic attenuation generally increases with frequency and so electronic noise will ultimately affect the frequency bandwidth that can be used for measurement.

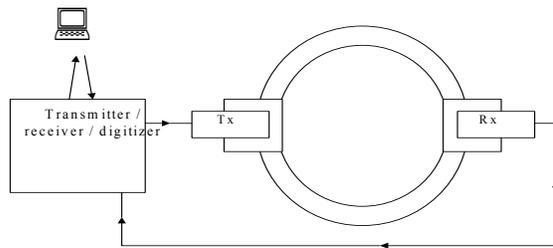


Figure 1: General outline of a typical ultrasonic system integrated into pipe-work.

If the properties of a test colloid affect the attenuation spectrum in a frequency range that is outside of the measurement bandwidth then those properties will not be accessible through ultrasonic measurement. We now relate measurable bandwidth to the noise properties of the ultrasonic system; the digitised received signal can be expressed in the frequency domain as

$$S(\omega) = S_o(\omega)e^{-\alpha(\omega)x} + N(\omega) \quad (5)$$

$S_o(\omega)$ is the transmitted signal and $N(\omega)$ represents the spectrum of the noise from all sources. Equation 5 can be manipulated to relate the relative error in an attenuation measurement to the noise to signal amplitude ratio ($NSAR = N(\omega)/S(\omega)$), see (Kalashnikov and Challis [10, 11]). We get

$$\frac{\Delta\alpha}{\alpha} = M(\alpha x) \times NSAR \quad (6)$$

Here M is a magnifying factor which depends on the total attenuation being measured (Nepers). It is multiplied by the noise term to give the relative error in measured attenuation. M is plotted versus (αx) on figure 2 from which it will be clear that the optimum measurement condition occurs at attenuations of around one Neper. Both high and low measured attenuations are associated with high errors as M increases. The practical limit is reached at measured attenuations between five and six Nepers.

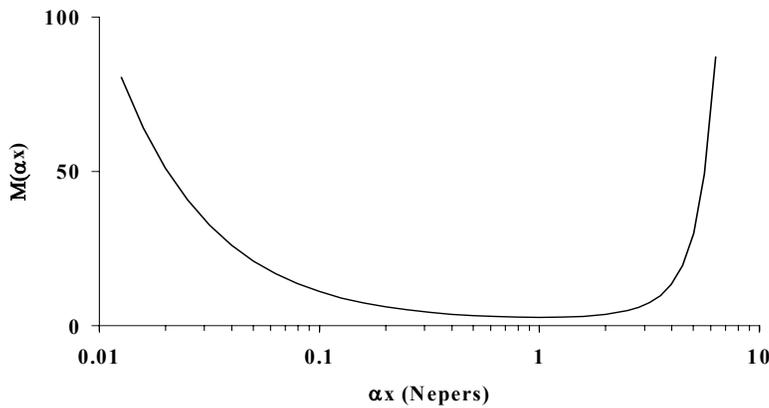


Figure 2: The magnifying factor $M(\alpha x)$, equation 4, plotted versus total attenuation (αx) .

Table 1 gives some examples of the maximum measurement frequency possible (f_{max}) when the distance between Tx and Rx is set at 50mm. Higher concentrations of dispersed phase would further reduce f_{max} roughly in proportion to concentration. Higher or lower transducer distances (eg process pipe diameters) with proportionately decrease or increase f_{max} . We illustrate how f_{max} limits estimates of PSD by the following example. Figure 3 shows the PSD of an oil in water emulsion obtained optically by *Mastersizer* (Malvern Instruments, UK). Superimposed on the figure is the PSD obtained with our laboratory ultrasonic system with operating bandwidth limited to 12 MHz. It is clear that the ultrasonic measurement gave a distribution over a similar range of particle sizes to that obtained by *Mastersizer* but lacking in the finer detail of bimodality.

Dispersed Phase	ϕ v/v	f_{max} MHz
Hexadecane	0.05	40
Polystyrene Spheres	0.30	30

Silica Spheres	0.08	10
AHR, T_iO_2	0.01	13

Table 1: Maximum measurable frequency (MHz) for various materials and dispersed phase concentrations ϕ when measurements are made across a 50 mm pipe.

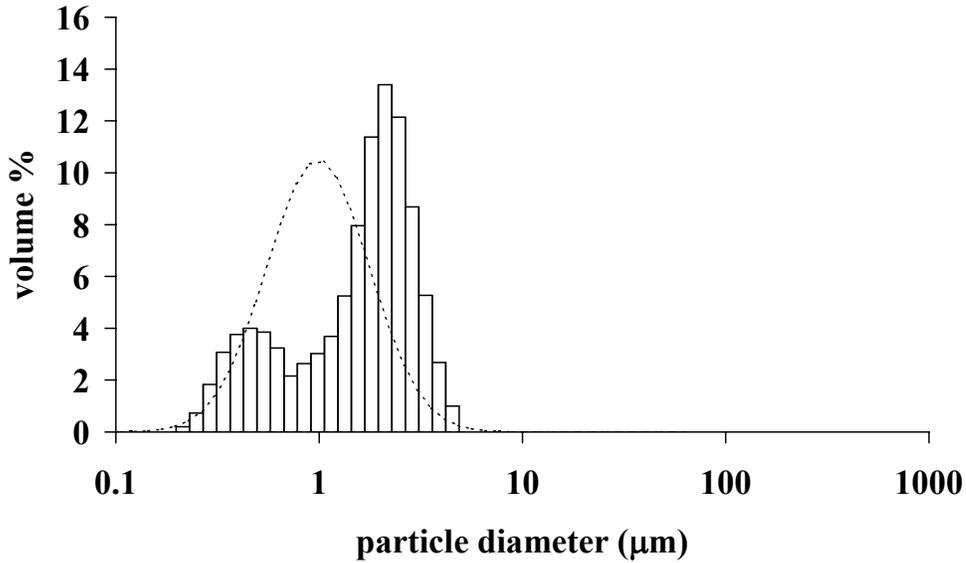


Figure 3: (a) PSD of an oil in water emulsion obtained by Mastersizer together with (b) the PSD estimated from ultrasonic measurement with bandwidth limited to 12 MHz - dotted line.

Figure 4 shows the ultrasonic attenuation spectrum calculated on the basis of equation 2 with the bimodal distribution from figure 3, and the attenuation spectrum for a single mode lognormal distribution fitted to the 3 – 12 MHz region of the bimodal attenuation spectrum. It will be clear from the figure that the ultrasonic attenuation ‘signatures’ of the two PSDs of figure 3 are virtually identical up to a frequency of around 20MHz. Only above this frequency can one size distribution be differentiated from the other. Successful estimation of the bimodal PSD would

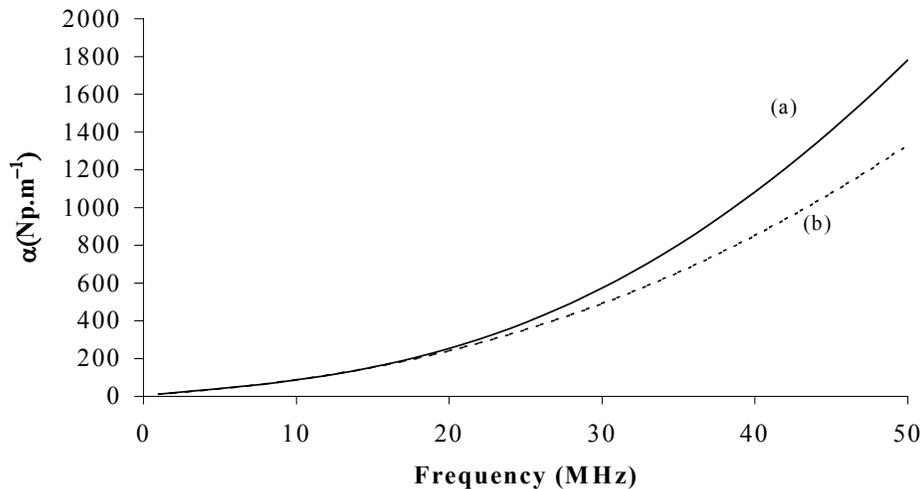


Figure 4: (a) The calculated spectrum from equation 2 and incorporating the bimodal distribution of figure 3. (b) the ultrasonic attenuation spectrum for an oil in water emulsion with a single mode distribution, fitted to the 3-12 MHz data from curve (a).

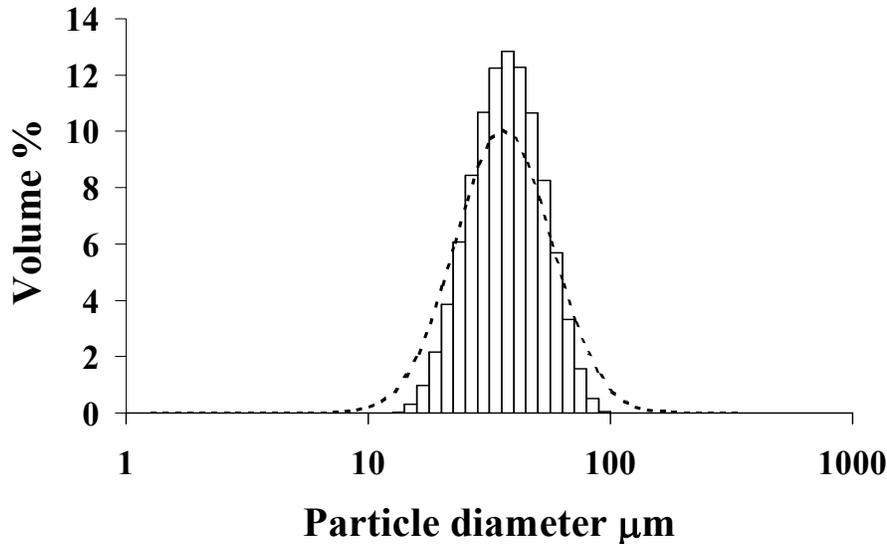


Figure 5: Particle size distribution (histogram) obtained using Mastersizer for a 3% w/w suspension of glass beads in water, together with a lognormal distribution function (dotted line) fitted to an ultrasonic attenuation spectrum of 30 MHz bandwidth.

require an ultrasonic signal bandwidth which extended up to 40MHz or so. In the general case where the available bandwidth is adequate for the PSD estimates required the ultrasonic technique can be shown to give results in excellent agreement with other methods such as laser diffraction. Figure 5 shows a comparison of an ultrasonic PSD estimate with that obtained by *Mastersizer* for a 3% w/w suspension of glass beads. The measurement bandwidth was 30 MHz.

System design: There are many factors associated with the design of a hardware system for on-line particle sizing on industrial plant. The gauge length between transmitting and receiving transducers is constrained by the diameter of the pipe or vessel to which the transducers will be attached. For most properly designed electronic systems there will be intrinsic noise levels that cannot be reduced by circuit modification. In most practical situations signal to noise ratios will be improved by coherent averaging of successive records taken from the receiver transducer; however, after each record time will be required to allow for acoustic reverberations to die down before the next record is taken, and this interval is typically in the range 10ms to 100ms, depending on the gauge length and the attenuation in the test medium. Intervals of this magnitude may not be possible where the test medium is flowing rapidly. There will also be a requirement for a minimum bandwidth over which the data is recorded so that features in the PSD such as bimodality can be adequately recognised. Against this background it is unlikely that a commercial system that is universally applicable will be feasible. The most likely product will be modular so as to be adaptable to a variety of process conditions. In order to arrive at the design of a system which meets the requirements of any particular process it will be necessary to carry out initial laboratory studies to establish the ultrasonic properties of the product to be monitored. These will be followed by computer modelling based on appropriate theories of ultrasonic propagation (such as ECAH) to investigate the sensitivity of ultrasonic data to potential changes in product properties and to establish the required measurement bandwidth. The error theory outlined above will then be used to establish the minimum and maximum possible gauge lengths between the

transducers and comparison of these with the dimensions of plant pipe-work will establish the overall feasibility of the monitoring scheme. Once feasibility is established there will be issues associated with the detailed design of the pipe and transducer assemblies and of the electronic system, both of which may be constrained by potential chemical, fire or explosion hazards.

Applications: The ultrasonic technique to monitor liquid particulate mixtures in process environments could, in principle, find applications in a wide range of industries; these may include lubricants, grinding materials, ceramics, speciality and agricultural chemicals, minerals, dyestuffs, paints and pigments, pharmaceuticals and food. Despite the apparent potential of the technique very few process applications have been documented in the public domain. One significant application to slurries in an industrial process has been reported by Scott *et al* of the E.I DuPont de Nemours Company in Delaware, USA [12]. Our own experience in applying the technique industrially is at present limited. We have built systems for monitoring the formation of agrochemicals flowing through pipes of diameters 6mm and 30mm; both were successful. We have also attempted (without success) to detect temper in molten chocolate flowing slowly in a process pipe of diameter 50mm. The very high absorption of ultrasound in chocolate required a gauge length of the order of 5mm and a pipe-mounted ultrasonic cell was built to achieve this: The chocolate was made to flow through horn shaped tubes on either side of the transducer mountings, changing from a 50mm diameter cylinder to a slit of 5mm height and 150mm width over a flow distance of 150mm.

Conclusion: Ultrasonic characterization of particulate mixtures in a plant setting is of moderate complexity and achievable at relatively low cost. The technique is no more complex than the optical methods incorporated in such instruments as the *Mastersizer*, although ultrasonic systems are at an earlier stage of development than their optical counterparts. It is important to note that ultrasonic systems have the advantage that they can probe optically opaque mixtures through pipes or vessels whose walls are opaque. The most significant limitation to the technique is that ultrasonic waves scatter strongly at bubbles and so ultrasonic monitoring may be unsuitable for processes in which significant volumes of gas are likely to be evolved. However, the evolution of gas and its recognition by ultrasound may in some circumstances be used as a monitor of reaction progress. In the majority of processes in which gas is not likely to form there is no impediment to routine monitoring of particulate suspensions on-line using ultrasound, provided that appropriate design procedures are followed.

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