

Acoustic Methods for Particle Characterisation[†]

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Abstract

Acoustic and Ultrasonic Methods for Particle Characterisation have many advantages. They are generally non-invasive, can be non-contact, are safe and often are economic. However, it can be difficult to interpret data, and the expertise and commercial equipment necessary may be in short supply and inappropriate to commercial requirements. Nevertheless the potential for these techniques is immense, particularly with regard to the newly emerging field of nanotechnology. A less well-recognised but just as important requirement is the ability to characterise systems on length scales between the molecular and the macroscopic. It is not so well known that acoustics can provide information over a huge range of length scales, from a few nanometres (ultrasound spectrometry) up to geological scales. Commonsense approaches to the understanding of acoustics obscure the potential of the modality. Scattering theory underpins all the theory of acoustic propagation, and adopting this initially theoretical approach indicates a world of new information. At one level particles and structures may be sized, at another their molar compressibility obtained, at another their shape determined. Acoustic methods are complementary to light scattering techniques offering advantages where light scattering does not work ? optically opaque systems, mixtures with small refractive index differences, for example. So ultrasound spectrometry is uniquely well-suited to the characterisation of nanoparticle concentrates. In this article the theory of ultrasound propagation is outlined simply for a general audience, emphasising those aspects which provide the greatest potential for adoption of the modality in the particle characterisation community and briefly describing the relevant current commercial and laboratory equipment.

Keywords: Acoustic, Ultrasound, Stability, Size, Size distribution

1. Introduction

There is a great variety of particle characterisation methods; of size, of size distribution, of density, of molecular weight and so forth. So why is another set of methods needed? It is recognised that an area where particle characterisation is deficient is with regard to very small particles in concentrated systems.

Clearly this is an issue in the area of nanoparticle production, for instance. There are other issues too, for example light scattering methods struggle if particles are coated, modifying their refractive index; or if there is more than one type of particle present. A good example of such a system which we have studied intensively is milk, which comprises several types of particles suspended in water. It is not difficult to satisfy yourself as to this fact, just compare skimmed and full-cream milk, both are white; this is because both the protein particles and the oil droplets are large and concentrated enough to scatter light, imparting a white colour on the product. Nevertheless, there must be powerful reasons to consider new techniques, invest in new equipment, train new experts

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and so on. But at a recent meeting of the Society of Chemical Industry in London it was baldly stated that there was no other technique to match ultrasound in the characterisation of nanoparticulate dispersions. Given the growing importance of this area we not surprisingly find a growing interest in ultrasound techniques for particle characterisation.

General introductions to ultrasound characterisation of particulate systems suspended in fluids can be found in works published by this author^{1,2)} and by Kinsler and Frey³⁾.

2. Equipment for Acoustic and Ultrasound Measurement

There is a great variety of equipment and equipment types available. Techniques are classified as continuous, quasi-continuous and pulsed, referring to the way in which the sound is generated. The most common type of sound transducer employs a piezoelectric ceramic called lead zirconium titanate (PZT); however there are many other types of construction including electrically polarized plastics, single crystal materials such as quartz or lithium niobate, each offering differing advantages. Single frequency, frequency scanning or broad-band (simultaneous multiple frequencies) generation of sound is possible, typically over frequencies between a few Hz and 100 MHz, although a much wider range is possible. Sample volumes may vary between a few hundred microliter in resonant cell systems operating over a limited frequency range of between 7 and 15 MHz to 500 ml in a quasi-continuous, frequency sweeping spectrometer (1 MHz to 200 MHz).

The acoustic set-up of a quasi-continuous frequency sweeping spectrometer is schematically represented in **Fig. 1**. One transducer transmits a sound pulse that passes through the sample medium and is

subsequently received by a second transducer. The sample medium is continuously stirred.

Ultrasound spectroscopy yields two types of measurable quantities; absorbance and velocity. Absorbance values A (in nepers) are derived from intensity measurements from the initial intensity $I_0(\omega)$ as a function of angular frequency ω ($= 2\pi f$) and the measured intensity $I(\omega)$:

$$A(\omega) = \ln \left[\frac{I_0(\omega)}{I(\omega)} \right] \quad [1]$$

The phase velocity is equal to the distance between the transducers, L , divided by pulse time of flight, Δt , of the sound pulse.

$$v(\omega) = \frac{L}{\Delta t(\omega)} \quad [2]$$

The experimental measurements are always carried out relative to reference samples and samples. This can be achieved directly doing only one measurement on the sample and one measurement on the reference sample under the same conditions. The relative absorbance measured is then called the excess absorbance and also leads to the excess absorbance coefficient α_{xs} . The excess absorbance coefficient (Nepers/m) is independent of the instrument set-up and is a material property.

$$\alpha_{xs}(\omega) \equiv [A_{sample}(\omega) - A_{reference}(\omega)]/2L \quad [3]$$

Here absorbance is normalised by the distance travelled by the pulse, in this case the first and second echoes are compared (**Fig. 1**) so the distance in this case is twice the cell width. It has been found that the measurement of the apparent excess absorbance can be carried out rapidly by selecting a suitable reference medium. The excess absorbance, α_{xs} is the absorbance that the sample exhibits over and above that of the reference sample. Usually water

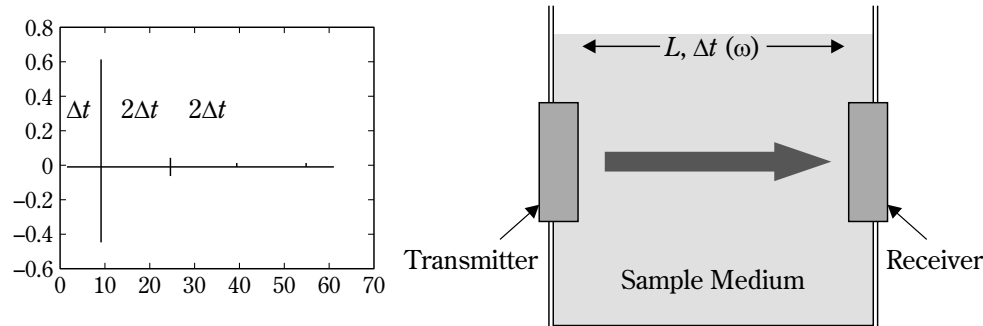


Fig. 1 Schematic representation of the spectrometer cell and pulse delay determination. Note that following the first 'echo', subsequently received echoes are reflected from the transmitter and consequently travel twice the distance taking twice the time.

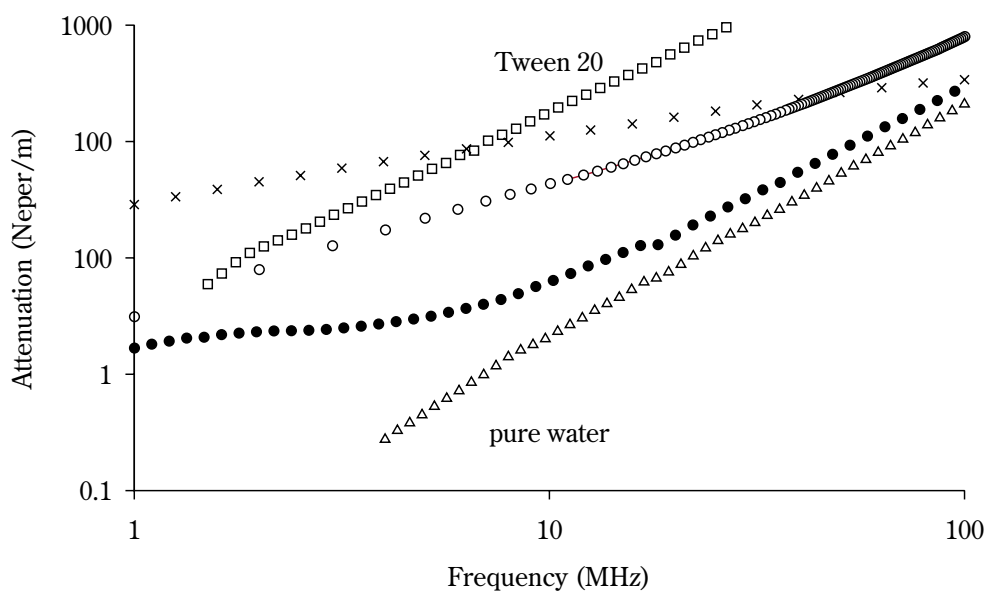


Fig. 2 Ultrasound attenuation plotted as a function of frequency for a surfactant solution, pure water, n-hexadecane and homogenised milk with a fat globule size of $1\ \mu\text{m}$ at 25°C . Water displays a power dependence on frequency of 2.01 and a pre-exponential factor of 0.02 whilst undiluted Tween 20 has an exponent of 1.69 and a pre-exponential factor of 3.59. Open triangles show the measured data in water purified by Millipore apparatus and open squares show the data for Tween 20. The open diamonds show the data for 4% Tween 20 dispersed in water; crosses are data for 20% v/v n-hexadecane in water, $D[3,2] = 1000\ \text{nm}$; circles are milk fat in water emulsion. (Data courtesy of Ran Huo, Valerie Pinfield and Stefan Meyer⁴), University of Leeds).

is used as the reference sample. It is a more direct measure of processes that happen in the sample of interest and not in the reference sample. By choosing an appropriate reference sample, other effects can be selectively excluded.

One issue regarding ultrasound particle sizing has been the quantity of material needed to make the measurements, one well-known spectrometer requiring 500 ml. The reason for this is the requirement in ultrasound particle sizing for a very large frequency range of more than two decades. The attenuation of sound intensity as a function of distance is roughly proportional to the square of the frequency, so high frequencies require much shorter path lengths in order for a good signal-to-noise ratio, as compared with low frequencies. In water for example, measurements at 100 MHz require a few millimetres whilst at 1 MHz, hundreds of millimetres are required.

Water has one of the lowest attenuation factors of any liquid and it is quite a challenge to accurately measure the attenuation at low frequencies. In **Fig. 2** is plotted the spectrum of water purified in a millipore apparatus as measured in our laboratory on a Malvern Ultrasizer (Malvern Instruments, Malvern, UK). Note that in this instrument, the lowest measurable attenuation is around $0.1\ \text{Neper m}^{-1}$ and the highest is around $1000\ \text{Neper m}^{-1}$. The instrument achieves

this huge dynamic amplitude and frequency range through a combination of electronics and changing path length between transducers. In the case of the Malvern Ultrasizer, the measured attenuation spectrum is an absolute one, whereas in the case of other instruments, the spectrum is relative to a reference material. A wide frequency and attenuation range is essential if accurate particle sizing is to be done in a significant range of liquids and suspensions.

The need for a wide frequency range is illustrated in **Fig. 2** for a selection of materials. Note that while the pure materials (water and Tween20) exhibit straightforward power law dependence on frequency, the dispersions (Tween20 in water, homogenised milk and n-hexadecane in water) exhibit a far from straightforward frequency dependence. In the case of Tween20, the Tween micelles scatter sound by a thermal mechanism which has a complicated frequency dependence which nevertheless is predictable⁵ and with which the micelles can be sized⁶. The same is true of the milk and the casein nanoparticles in milk⁴. It is important to characterise the behaviour of the surfactant in the solvent if ultrasound particle sizing is to be carried out successfully.

Pulsed systems offer higher data acquisition rates, as high as ten measurements a second but lower bandwidths. Nevertheless, if averaged data is

required, for example particle compressibility, solid content or a trend in size due to coalescence, then limited bandwidth, pulsed systems may be the best choice. An example of a miniaturised, limited bandwidth spectrometer using pulse techniques is given in reference⁷. A broadband transducer (1-10MHz) excites a pulse in a buffer rod within which it reverberates. Some of the sound escapes from the buffer rod into the sample within which it also reverberates; the same transducer both exciting and detecting the sound pulses. Comparison of the reverberation within the buffer rod and in the sample gives accurate velocity and attenuation data.

An even simpler system simply measures the reverberation time of sound pulses in a sample between pipe walls, generated and detected by the piezoelectric transducer embedded in the wall. This is a simple and robust system that can operate inline and be temperature-cycled between -15°C and 90°C, so is particularly suitable for crystallization studies^{8,9,10}.

3. Sizing nanoparticles

Solid particles can also be sized with attenuation spectroscopy. In **Fig. 3** is plotted the attenuation of sound at various frequencies between 100 kHz and 200 MHz for silica monodispersions of various sizes. Comparing **Fig. 3** with **Fig. 2** we may note that we have plotted the results obtained within the dynamic range of the Malvern Ultrasizer. Firstly note the complicated dependence on both size and frequency. This occurs because there are three scattering mechanisms at work, i.e. thermal scattering, visco-inertial

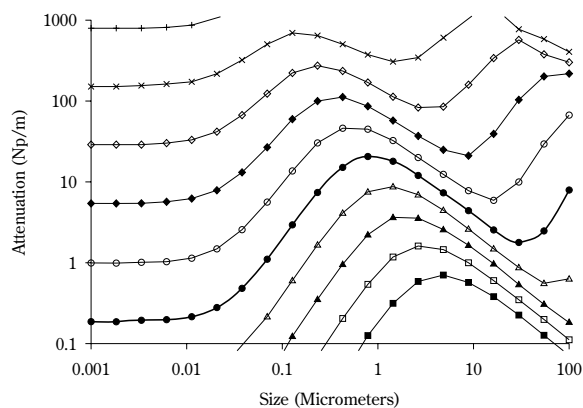


Fig. 3 Attenuation plotted against size and frequency for 2.24% v/v monosize silica suspended in water. Solid squares, 0.1 MHz; open squares, 0.233 MHz; solid triangles, 0.541 MHz; open triangles 1.26 MHz; closed circles, 2.93 MHz; open circles, 6.82 MHz; closed diamonds, 15.87 MHz; open diamonds, 36.94 MHz; crosses, 85.95 MHz; pluses, 200 MHz.

scattering and elastic scattering, in addition to the frequency dependence of the attenuation inherent in each phase out of which the dispersion is composed. The width of the scattering peaks arises from the non-propagational nature of the thermal and shear waves which are excited by the particle in the acoustic field, the decay lengths of these waves scales inversely as the square root of the frequency. The situation is further complicated by multiple scattering which is responsible for the significant differences between the data for the dilute silica suspension in **Fig. 3** and the data for the concentrated suspension in **Fig. 4**; nevertheless, current ultrasound scattering theory is capable of predicting this behaviour from first principles⁵. In general, as the frequency increases so does the attenuation, as to be expected. However, this does not occur simply. Examination of **Fig. 3** indicates that little information about size distribution can be obtained for sizes below around 10 nm. But this does not mean that particles smaller than this are not detected. In fact a big advantage of ultrasound is that particles of all sizes are detected and contribute to the volume fraction, which is obtained independently from the spectra. So we can expect to obtain accurate values of the volume fraction, regardless of the size distribution. Examination of **Fig. 3** also indicates that the spectrum is very sensitive to particle size in the region 10 nm to 500 nm. In general there may not be a unique solution to the spectral inversion; several size distributions may satisfy a given spectrum. Here modelling of the spectrum is very useful because this allows a-priori knowledge of the distribution to constrain the range of solutions to the spectral inversion. Note in **Fig. 4** how increasing particle concentration increases the sizing range considerably.

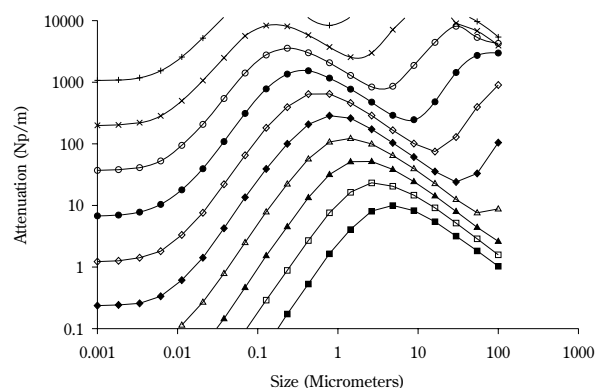


Fig. 4 Attenuation plots for 30% v/v monosize silica in water. Symbols as in **Fig. 3**.

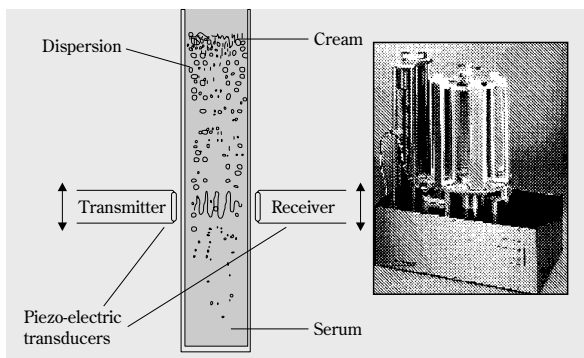


Fig. 5 Acoustiscan ultrasound scanner, diagram on left, picture on right¹¹.

4. Stability of Particulate Systems

The stability of particle dispersions is of particular concern to manufacturers and acoustic techniques offer a unique combination of ability to non-invasively characterise concentrated dispersions and to provide data which can be compared with mathematical models. This combination of techniques offers the prospect of product lifetime prediction, sometimes called shelf life^{12, 13, 14, 15, 16, 17}. The Acoustiscan scanner (Fig. 5) employs a pulse echo technique similar to that of the FSUPER (Frequency scanning ultrasonic pulse echo reflectometer⁷). In the case of the Acoustiscan though, the transducers are moved using a stepper motor system, building up a spatial and temporal picture of the distribution of particles.

In Fig. 6 the behaviour of an emulsion in which the density difference between the lighter dispersed

phase and the heavier aqueous phase results in creaming is shown. We have shown that this type of behaviour is completely described by buoyancy and hydrodynamics and can model the behaviour precisely¹³. Fractionation occurs as the smaller particles are moved upwards in the backwash of the larger faster moving particles, resulting in the blurred-out interface between the cream (top) and the serum (bottom). This type of instability is actually unusual, largely because the particles interact through a variety of mechanisms - depletion flocculation, van der Waals forces, ionic forces, bridging flocculation, etc. In this case it is much harder to model the behaviour; an example of an emulsion which gels through depletion flocculation is given in Fig. 7. Note that there is a well-defined boundary between the cream and the serum; this arises because particles of all sizes are held within the flocs which then cream together, preventing the fractionation process seen in Fig. 6. This technique and approach permits the rapid prediction of dispersion stability because it is sensitive to the microscopic changes occurring which lead to product destabilisation.

5. Particle State and Solid Content

The speed of sound is extremely sensitive to the crystalline state of particles^{8, 10}. This is because there is a large change in compressibility between the liquid and solid state. The density change is nothing like so great and as a result, we see a big change in the speed of sound through $v = 1/\sqrt{\kappa\rho}$. Since the speed of sound is measured in the UVM system with a pre-

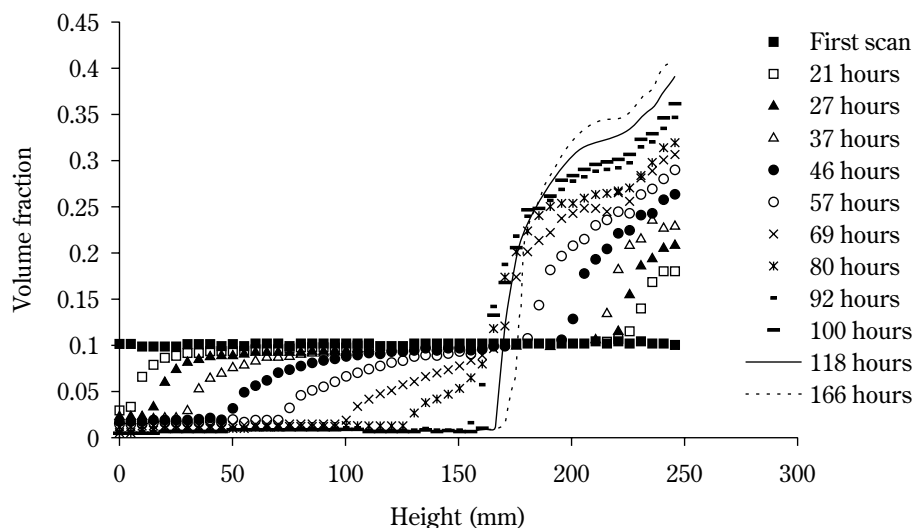


Fig. 6 Unhindered creaming of an oil-in-water emulsion measured using the Acoustiscan.

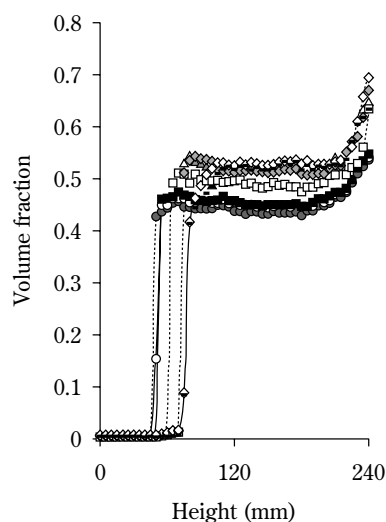


Fig. 7 Creaming and gelation in a flocculating oil-in-water emulsion. 35 wt % n-tetradecane oil-in-water emulsions containing 4 wt % sodium caseinate, 30 C, pH 6.8 . 0.5 μ m. ●, after 52 h; ○, after 64 h; ■, after 3 d; □, after 6 d; *, after 12 d; △, after 15 d; ▼, after 19 d; ◇, after 33 d.¹⁴⁾

cision of 0.1 ms⁻¹ in 1500, we determine solid content to within 0.01 v/v or 1% v/v, regardless of particle size. This is a simple, rapid (10 measurements per second) and accurate method for determining particle state in concentrated dispersions of particles, no matter what their size. **Fig. 8** shows the solid content determined in a crystallisation n-hexadecane emulsion whose oil phase crystallizes at 2°C and melts at 18°C. This emulsion is very stable and can be cycled again and again between the crystalline and liquid states (**Fig. 9**). The method can distinguish between crystallization and the formation of a glass, since the two states of matter have totally different compressibilities.

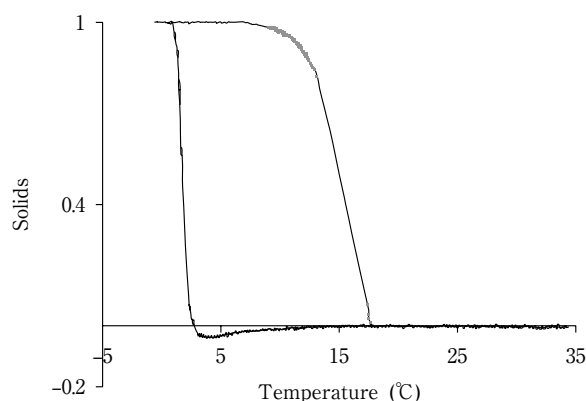


Fig. 8 Solid content of a 5% v/v n-hexadecane oil-in-water emulsion with D[3,2] = 123 nm.

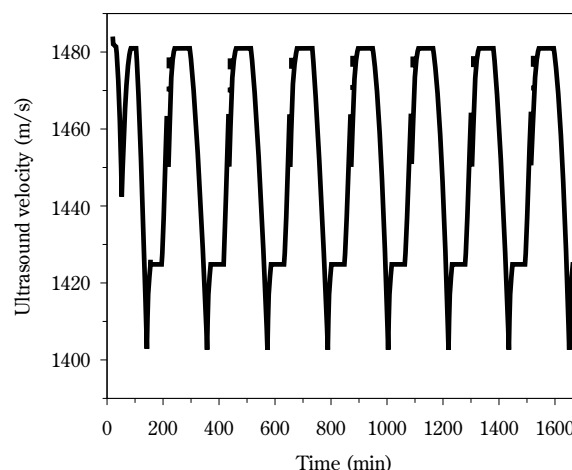


Fig. 9 Velocity data for the emulsion in ... cycled continuously between 0°C and 40°C, 7 times.

6. Conclusion

It is indeed surprising that ultrasound measurement is not used more widely in particle characterisation. This is particularly true when it is considered that for applications such as concentrated nanoparticle dispersions, there is no other technique which can be used to determine the state of the particle, the state of its surface or its size distribution. Nor is there any rival in the area of crystallization, particularly in the initial stages during nucleation. The answer to this question lies in the lack of commercially available equipment properly adapted to the needs of industry. However, such a situation is unlikely to last since the hurdles are not technical but practical. Equipment needs to become more versatile, more adaptable to manufacturing needs and less expensive; this is just a matter of time.

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Author's short biography



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Malcolm Povey was born in 1947 in Wallasey, England. He studied physics at Lancaster University, graduating with a BA in 1970 and a PhD in 1973. He spent his postdoctoral period at Leeds University researching the effects of very high pressure on the bandstructure of alkali metal alloys and transferred to Food Science at Leeds in 1976. In Food Science he applied acoustical methods to the testing and evaluation of foods such as eggs, fruit, biscuits and milk.

Co-inventor of the 'Ultracane' and the Baker Petrolite 'Aggregation Monitor', he is internationally recognised as a leading researcher in the area of ultrasound, having pioneered its application to food. In 2003 his achievements were recognised by promotion to the Chair of Food Physics at Leeds.

Current research projects include nanoparticles for anti-microbial materials, nanocrystals, acoustic microscopy, product stability assessment, acoustics and ultrasonics for materials testing and novel ultrasound methods for characterising proteins. Most recently he developed in conjunction with Stable Microsystems methods for acoustically assessing the mechanical properties of materials including crispy foods such as biscuits.

He chairs the Hahn Prize Committee, the pre-eminent European food engineering and science prize.