Ultrasonic Measurements in Particle Size Analysis

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The particle size distribution and concentration of a colloidal dispersion can be determined by measuring its ultrasonic velocity and/or attenuation coefficient as a function of frequency and then using a suitable mathematical model to interpret the spectra. Ultrasonic spectroscopy can be used to analyze particle sizes between about 10 nm and 1000 μm, and is suitable for application to concentrated systems (often up to 50 wt%). This technique has considerable advantages over many alternative technologies because it can be applied to systems that are optically opaque without the need of any sample preparation.

1 INTRODUCTION

Ultrasonic spectroscopy utilizes measurements of the frequency dependence of the ultrasonic velocity and/or attenuation coefficient of colloidal dispersions to obtain information about the concentration and size distribution of colloidal particles. The velocity (c) at which an ultrasonic wave propagates through a particulate suspension, and the amount by which it is attenuated (α), are governed by interactions between the ultrasonic wave and the particles, e.g. transmission, reflection, absorption, and scattering. Ultrasonic attenuation spectroscopy (UAS) is more commonly used than ultrasonic velocity spectroscopy (UVS), although both methods can provide similar information. Ultrasonic spectroscopy has advantages over many existing particle-sizing technologies because it is non-destructive and non-invasive, is capable of rapid measurements and can be used to characterize systems which are concentrated and optically opaque. Ultrasonic spectroscopy is sensitive to particles with radius between about 10 nm and 1000 μm. The maximum particle concentration which can be analyzed varies between about 10 and 50 wt% depending on the nature of the system. On the other hand, the technique is unsuitable for analyzing dilute suspensions, i.e. particle concentrations below about 1 wt%. The other major limitations of the technique are that air bubbles can interfere with measurements and that a large amount of information about the thermophysical properties of the component phases are needed to interpret ultrasonic spectra.

There are two major steps in the determination of particle size using ultrasonic spectroscopy: (i) measurement of the ultrasonic velocity and/or attenuation spectra of the colloidal dispersion and (ii) interpretation of the resulting spectra using a suitable theory. To obtain accurate measurements it is necessary to carry out both steps carefully.

2 MEASUREMENT TECHNIQUES

Determination of the particle size distribution of a colloidal dispersion relies on being able to measure the frequency dependence of the ultrasonic velocity and/or attenuation coefficient.[1-3] The ultrasonic velocity is the distance the ultrasonic wave moves through the sample per unit time, whereas the attenuation coefficient is a measure of the decrease in the amplitude of the ultrasonic wave per unit distance traveled. The ultrasonic velocity can be determined by two different methods: (i) measuring the time, t taken for a pulse of ultrasound to travel a known distance, x: $c = x/t$, or (ii) measuring the wavelength of an ultrasonic wave, λ, at a known frequency, f: $c = \lambda f$. The attenuation coefficient is determined by measuring the reduction in amplitude of an ultrasonic wave which has traveled a known distance through a material (Equation 1):

$$\alpha = -\frac{1}{x} \ln \frac{A_x}{A_0} \tag{1}$$

where A_0 is the initial amplitude of the ultrasonic wave ($x = 0$), and A_x is the amplitude after it has traveled a distance x.

To cover a wide range of particle sizes it is necessary to measure the ultrasonic properties of a colloidal dispersion over a wide range of frequencies.[2] Commercial ultrasonic particle-sizing instruments typically make measurements over the range 1 to 200 MHz, which enables them to analyze particles between about 10 nm and 1000 μm in radius. This range can be extended by using custom-built techniques to carry out measurements at higher or lower frequencies.[4–7]

The frequency dependence of the ultrasonic properties of colloidal dispersions can be determined using a number of different measurement principles.[4–8] The major difference between them is the form in which the ultrasonic signal is applied to the sample, i.e. continuous wave, tone-burst or pulse (Figure 1). Nevertheless, the experimental apparatus used in the different techniques is usually fairly similar, consisting of a signal generator, a signal analyzer and a measurement cell (Figure 2).
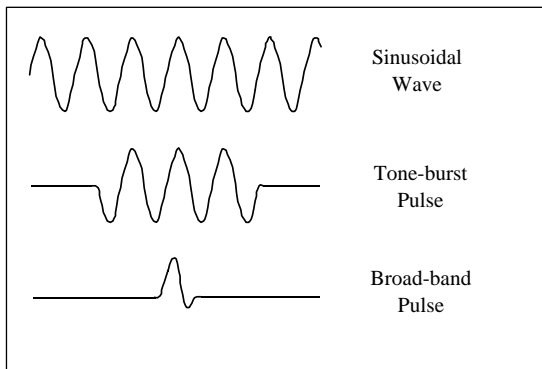

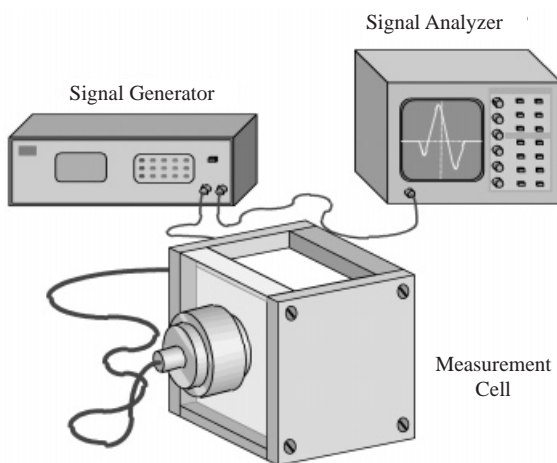**Figure 1** Different types of signal used in the ultrasonic analysis of colloidal dispersions.

Figure 2 A typical ultrasonic spectrometer consists of a signal generator, a signal analyzer and a measurement cell.
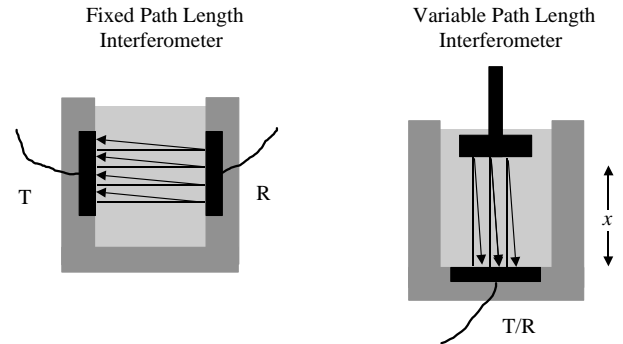

Figure 3 An interferometer used to measure the frequency-dependent ultrasonic properties of liquids may be of the fixed path length or moveable path length type.

2.1 Continuous Wave Techniques

Ultrasonic spectrometers which utilize continuous waves are usually referred to as *interferometers*.[9] Interferometry of liquids can be carried out using two different types of experimental arrangement: fixed path length and variable path length (Figure 3).

2.1.1 Fixed Path Length Devices

In a fixed path length (or resonator) device, the sample to be analyzed is placed in a thermostated measurement cell between two parallel piezoelectric ultrasonic transducers: a transmitter and a receiver. A signal generator produces an electrical sinusoidal wave of appropriate frequency and amplitude. This wave is applied to the transmitter where it is converted into a sinusoidal ultrasonic wave that propagates into the sample. The ultrasonic wave undergoes multiple reflections between the two transducers which results in the formation of a stationary wave. The signal detected by the receiving transducer is amplified and relayed to a signal analyzer. The amplitude of the received signal goes through a series of maxima and minima, due to constructive and destructive interference, when the frequency of the ultrasonic wave is varied. The ultrasonic velocity and attenuation coefficient are determined by analyzing the resulting amplitude versus frequency spectra.

To a first approximation the attenuation per cycle ($\alpha\lambda$) is given by Equation (2):

$$\alpha\lambda = \pi \frac{\Delta f_N}{f_N} \qquad (2)$$

where f_N is the central frequency of a maxima and Δf_N is the width of the maxima at -3 dB, whilst the ultrasonic velocity is given by Equation (3):

$$c = 2d\Delta f \qquad (3)$$

where d is the path length of the measurement cell and Δf is the frequency difference between the central frequencies of two successive maxima.

2.1.2 Variable Path Length Devices

In a variable path length device the sample to be analyzed is placed in a thermostated measurement cell which usually contains an ultrasonic transducer and a moveable reflector plate. A signal generator produces a sinusoidal electrical wave of the appropriate frequency and amplitude which is applied to the ultrasonic transducer where it is converted into a sinusoidal ultrasonic wave. The ultrasonic wave propagates into the sample and undergoes multiple reflections between the transducer and reflector plate which results in the formation of a standing wave. When the distance between the transducer and reflector plate is varied the amplitude of the signal received by the transducer goes through a series of maxima and minima because of constructive and destructive interference. The distance between successive maxima (Δd) is equal to half the ultrasonic wavelength of the sample, and so the ultrasonic velocity can be calculated: $c = f\lambda = 2f\Delta d$. The amplitudes of the maxima decrease as the distance between the reflector plate and transducer is increased because of attenuation by the sample. The attenuation coefficient is determined from Equation (1) by measuring the amplitude of the maxima as a function of the separation between the reflector plate and transducer.

2.2 Pulse Techniques

Ultrasonic spectrometers that utilize pulse techniques may be operated in a *pulse-echo* or *through-transmission* mode.[8,9] In the pulse-echo mode a single transducer is used to both transmit and receive the ultrasonic signal, whereas in the through-transmission mode separate transducers are used to transmit and receive the signal (Figure 4).

2.2.1 Through-transmission Techniques

The sample to be analyzed is placed in a thermostated measurement cell between two ultrasonic transducers: a transmitter and a receiver (Figure 4). The transmitting transducer produces a pulse of ultrasound which travels across the sample and is detected by the receiving transducer. The ultrasonic velocity and attenuation coefficient of the sample are determined by measuring the time-of-flight (Δt) and amplitude (A) of the ultrasonic pulse which has traveled across the sample. The ultrasonic velocity is equal to the length of the sample, d, divided by the time required to travel this distance: $c = d/\Delta t$. The attenuation coefficient is calculated by
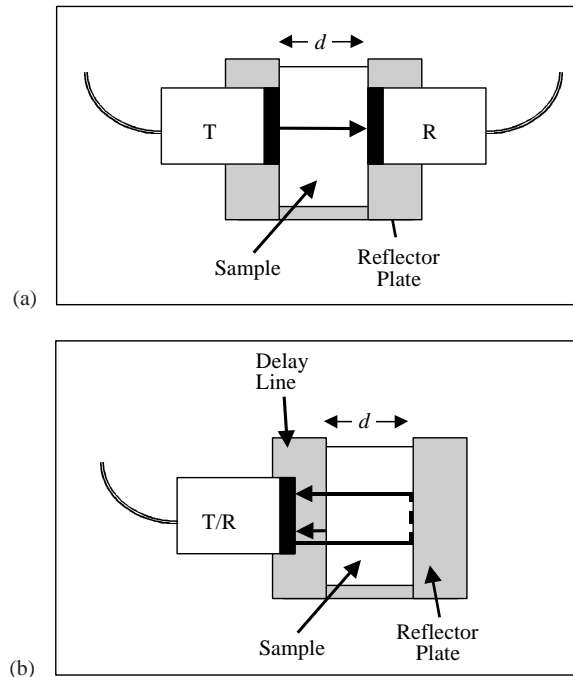

Figure 4 The ultrasonic properties of a colloidal dispersion can be determined using pulsed techniques by (a) the through-transmission or (b) the pulse-echo methods.

comparing the reduction in the amplitude of the pulse that has traveled through the sample with that of a pulse which has traveled through a calibration material: $\alpha_s = \alpha_c - \ln(A_s/A_c)/d$, where the subscripts c and s refer to the properties of the calibrant and sample, respectively. To obtain accurate attenuation measurements it is necessary to ensure that the measurement cell is well designed to minimize temperature fluctuations, reverberation of ultrasonic pulses in cell walls and transducers, diffraction effects and phase cancellation due to nonparallel walls.[8]

The frequency dependence of the ultrasonic properties of a sample can be obtained using two different approaches: (i) the Fourier Transform (FT) method, and (ii) the tone-burst method. For both approaches, a pair of ultrasonic transducers is used which is capable of generating ultrasonic energy over a wide range of frequencies. These *broad-band* transducers contain piezoelectric crystals whose oscillation is highly damped by attaching a backing material to the crystal.

In the FT method, a signal generator is used which is capable of producing a broad-band electrical pulse which contains a wide range of frequencies.[9–11] This pulse is applied to the transmitting transducer where it is converted into a broad-band ultrasonic pulse. After this pulse has traveled through the sample it is detected by the receiving transducer, and then digitized and stored. The

frequency dependence of the magnitude and phase of the pulse are determined using a FT technique. The ultrasonic velocity is then determined from the phase, whilst the attenuation coefficient is determined from the magnitude. To cover the whole frequency range it is often necessary to use two or three pairs of broad-band transducers with different central frequencies. Ultrasonic velocity and attenuation spectra are acquired much more rapidly using FT pulse techniques than continuous-wave techniques. This is because the whole of the frequency range is measured by propagating a pulse through the sample, rather than having to make measurements separately at each individual frequency.

In the tone-burst technique, a signal generator is used which is capable of generating tone-burst pulses over the required frequency range. A "tone-burst" is a single pulse which contains a number of cycles of ultrasound at a fixed frequency (Figure 1). A tone-burst pulse of a particular frequency is applied to the transmitter, and then the magnitude and phase of the tone-burst pulse that travels through the sample and is detected by the receiver are measured.[12] The ultrasonic attenuation coefficient is determined by measuring the amplitude of the received signal, whilst the ultrasonic velocity is determined by measuring the change in the phase of the received signal. An ultrasonic spectrum is acquired by repeating this process for a number of frequencies. Because measurements are carried out separately at each frequency, this approach is more time-consuming and laborious than the FT method.

2.2.2 Pulse-echo Techniques

The frequency-dependent ultrasonic properties of a sample are measured in a very similar fashion as in the through-transmission technique, except that a single transducer is used to both transmit and receive the ultrasonic pulses (Figure 4). The ultrasonic transducer generates a pulse of ultrasound which travels across the sample, is reflected from the back wall of the measurement cell, travels back through the sample, and is then detected by the same transducer. The velocity and attenuation coefficient are calculated in exactly the same manner as described for the through-transmission technique, expect that the pulse has now traveled a distance $2d$ rather than d.

To obtain accurate and reliable measurements it is important to take extreme care in designing and manufacturing measurement cells, for all types of ultrasonic technique. Some of the most important factors to consider are nonparallelism of surfaces, imperfect reflection at boundaries, reverberations in cell walls, temperature fluctuations and diffraction losses.[8]

3 PARTICLE-ULTRASONIC WAVE INTERACTIONS

A knowledge of the physical basis of the various forms of interaction between ultrasonic waves and particles is necessary to understand how ultrasound can be used to measure particle size.[1−3,8] The four most important types of interaction between an ultrasonic wave and a colloidal dispersion are listed below.

3.1 Intrinsic Absorption

Each of the individual component phases in a colloidal suspension absorbs ultrasound as a result of classical (viscous and thermal) and relaxation loss mechanisms. These losses are determined by the composition of the suspension, rather than by its microstructure. The magnitude of these losses can be calculated by measuring the ultrasonic absorption coefficients of the individual components.

3.2 Visco-inertial Dissipation Losses

In the presence of an ultrasonic wave a particle oscillates backwards and forwards because it has a different density to that of the surrounding liquid. This oscillation is damped by the viscosity of the surrounding liquid, which causes some of the ultrasonic energy to be converted to heat, and therefore leads to a reduction in the amplitude of the ultrasonic wave. The magnitude of these visco-inertial losses increases as the density difference between the droplet and surrounding liquid increases. Visco-inertial dissipation losses depend on the size of the droplets in a colloidal suspension.

3.3 Thermal Dissipation Losses

In the presence of an ultrasonic wave the temperature of a particle periodically increases and decreases relative to that of the surrounding liquid because of differences in the thermal properties of the continuous and disperse phases. The temperature gradient which arises at the particle surface causes a net flow of heat out of the droplet, which leads to a reduction in the amplitude of the ultrasonic wave, i.e. some of the energy initially stored in the ultrasonic wave is converted to heat. The magnitude of these losses is governed by the difference in thermal properties between the droplet and the surrounding liquid, e.g. thermal expansion coefficient, specific heat capacity and thermal conductivity. Thermal dissipation losses depend on the size of the droplets in a colloidal suspension.

3.4 Scattering Losses

The pulsation and oscillation of a particle in the presence of an ultrasonic wave causes the generation of secondary ultrasonic waves by the particle. Thus some of the ultrasonic energy associated with the incident wave is redirected into different directions, and an increase in the attenuation coefficient may be detected. Scattering losses are usually negligible in the long wavelength limit ($r \ll \lambda$), but become dominant when the particle size is of the same order of magnitude as the ultrasonic wavelength. Scattering losses depend on the size of the droplets in a colloidal suspension.

To a first approximation, the overall attenuation coefficient of a colloidal suspension can be considered to be the sum of these various contributions (although in reality some of these mechanisms are coupled to each another). In most suspensions, one or two of the above mechanisms usually dominate the overall attenuation in a particular frequency range. At relatively low frequencies, the visco-inertial and thermal loss mechanisms usually dominate, but at higher frequencies the intrinsic absorption and scattering losses usually dominate.

4 ULTRASONIC SCATTERING THEORY

Once the ultrasonic velocity and/or attenuation spectra of an emulsion have been measured it is necessary to convert them into a particle size distribution using an appropriate theory. Theories are based on a mathematical treatment of the physical processes that occur when an ultrasonic wave propagates through an ensemble of particles suspended in a fluid.[1-3] One of the most comprehensive models (Equation 4) is based on multiple scattering theory:[13]

$$\left(\frac{K}{k_1}\right)^2 = 1 + \frac{4\pi N f(0)}{k_1^2} + \frac{4\pi^2 N^2}{k_1^4}(f^2(0) - f^2(\pi)) \quad (4)$$

where $f(0)$ and $f(\pi)$ are the *scattering amplitudes* of the individual droplets (Equations 5 and 6):

$$f(0) = \frac{1}{ik_1} \sum_{n=0}^{\infty}(2n+1)A_n \quad (5)$$

$$f(\pi) = \frac{1}{ik_1} \sum_{n=0}^{\infty}(-1)^n(2n+1)A_n \quad (6)$$

Here $K(= w/c_S + i\alpha_S)$ is the complex propagation constant, c_S is the ultrasonic velocity and α_S is the attenuation coefficient of the colloidal suspension. k_1 is the complex propagation constant of the continuous phase ($= w/c_1 + i\alpha_1$), ϕ is the disperse phase volume fraction, $w(= 2\pi f)$ is the angular frequency f is the frequency,

$i = (-1)^{1/2}$, and r is the droplet radius. The A_n terms are the *scattering coefficients* of the various types of waves scattered from the individual droplets, e.g. monopole (A_0), dipole (A_1), quadrupole (A_2) etc.

Approaches for calculating the scattering coefficients of both fluid and solid particles are available in the literature.[14,15] The most rigorous approach calculates the A_n terms by solving a series of 6×6 complex linear simultaneous equations at each value of n, although simpler analytical expressions are available in the long wavelength limit.[14,15] The values of the scattering coefficients depend on the relative thermophysical properties of the component phases, the ultrasonic frequency used and the size of the emulsion droplets. The terms containing ϕ in Equation (4) describe single scattering effects, whilst the terms containing ϕ^2 describe multiple scattering effects. Multiple scattering becomes increasingly important as the concentration of droplets in a colloidal suspension increases.

For a colloidal suspension containing polydisperse particles the above equation must be modified (Equation 7):

$$\left(\frac{K}{k_1}\right)^2 = 1 + \frac{4\pi}{k_1^2} \sum_j N_j f_j(0) + \frac{4\pi^2}{k_1^4} \sum_j N_j^2 \left(f_j^2(0) - f_j^2(\pi)\right)$$

$$(7)$$

where the subscript j refers to the property with droplet size r_j. This equation can be used to relate the ultrasonic properties of a colloidal suspension (velocity and attenuation coefficient) to its thermophysical properties, composition (ϕ) and particle size distribution.

Recently, it has been shown that the above theory must be modified to take into account interactions due to overlap of viscous[16] and thermal waves[17] generated by the particles. These interactions cause large deviations between the classical multiple scattering theory and experimental measurements at low ultrasonic frequencies, small droplet sizes and high droplet concentrations.

5 INTERPRETATION OF ULTRASONIC SPECTRA

To determine the particle size distribution of a colloidal dispersion one usually measures its ultrasonic velocity and/or attenuation coefficient as a function of frequency. The particle size distribution is then determined by finding the droplet size distribution that gives the best fit between the predictions of the ultrasonic scattering theory and the experimental ultrasonic spectra.[1,2] There are two approaches to solving this inverse scattering problem: *model-independent* inversion and *model-dependent* inversion. In the model-dependent inversion method it is assumed that the particle size distribution follows some

common form which can simply be modeled mathematically, e.g. log-normal (Equation 8).

$$P(r) = \frac{1}{x_g \ln \sigma_g \sqrt{2\pi}} \exp{-\left(\frac{\ln^2 \sigma_g}{2}\right)} \exp\left(\frac{[\ln r - \ln x_g]^2}{2 \ln^2 \sigma_g}\right) \tag{8}$$

where $P(r)$ is the probability of having a particle of radius r, x_g is the geometric mean of the radius and σ_g is the standard deviation of the geometric mean. The droplet size distribution can then be characterized by only two parameters: x_g and σ_g. The geometric mean and standard deviation which give the best agreement between the measured and predicted ultrasonic spectra are found by a least squares analysis. Most commercial ultrasonic instruments assume that the particle size distribution follows either a monomodal or bimodal log-normal distribution.

In the model-independent analysis no a priori assumption is made about the form of the particle size distribution. Although this method is scientifically more satisfactory, because many suspensions do not have particle size distributions which can be described by simple mathematical expressions, it is extremely time-consuming to compute. In addition, there are sometimes situations where a number of different particle size distributions give an equally good agreement between theory and experiment and it is not possible to decide which is correct.

6 APPLICATIONS

The ability of ultrasonic spectroscopy to determine the particle size distribution of colloidal suspensions has been demonstrated by many workers.[3,6,16,18−21] Fully automated particle sizing instruments which utilize ultrasonic spectroscopy are available commercially. These instruments are capable of measuring both the disperse phase volume fraction and particle size distribution of colloidal suspensions in a few minutes. For certain systems, these instruments are capable of characterizing suspensions containing high particle concentrations (sometimes as high as 60%).

The attenuation spectra of a series of corn oil-in-water emulsions with different disperse phase volume fractions (1–50 vol%) are shown in Figure 5. The particle size distribution and droplet concentration measured by the ultrasonic technique are tabulated in Table 1. There is excellent agreement between the measured and actual volume fractions of the emulsions up to the highest droplet concentration. In addition, the mean particle diameter is relatively insensitive to droplet concentration, indicating that the ultrasonic technique is capable of analyzing this system over a wide range of concentrations without any sample preparation. Nevertheless, it should
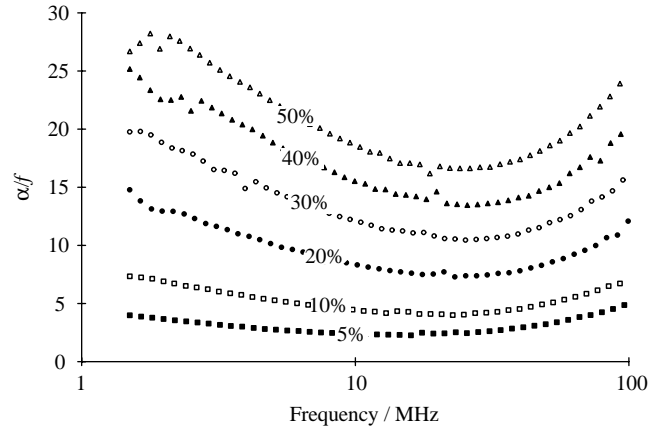
Figure 5 Ultrasonic attenuation spectra of corn oil-in-water emulsions containing different droplet concentrations. The particle size distribution and disperse phase volume fraction are determined by finding the values which give the best-fit between the measurements and ultrasonic scattering theory.

Table 1 Disperse phase volume fraction (ϕ), geometric mean (x_g) and standard deviation of the geometric mean (σ) of various corn oil-in-water emulsions determined by finding the best fit between ultrasonic scattering theory and the experimental measurements shown in Figure 5

Actual ϕ	Measured ϕ	x_g (μm)	σ
50	47.9	1.32	2.50
40	37.9	1.17	2.24
30	30.1	1.20	2.07
20	20.6	1.18	1.93
10	10.5	1.14	1.85
5	5.5	1.16	1.74
1	1.5	1.30	1.14

be noted that in systems where thermal or viscous overlap effects become important there may be quite large disagreements between the experimental data and the theories used to interpret them.[16,17]

7 PERSPECTIVE AND FUTURE DEVELOPMENTS

The ability of ultrasonic spectroscopy to characterize colloidal suspensions which are concentrated and optically opaque without the need for any form of sample preparation is extremely important for many applications. There are few other particle sizing technologies which are capable of analyzing this type of system and therefore it seems likely that the ultrasonic technique will find increasing applications in the future. One of the areas where the technique is most likely to be used is for the on-line

determination of particle size distributions of colloidal suspensions during processing. The ultrasonic technique could be used to monitor the efficiency of a processing operation in real time that could lead to a major improvement in the manufacture of many colloidal-based materials, e.g. foods, pharmaceuticals, petrochemicals, agrochemicals and cosmetics.

Despite its many advantages over alternative technologies there are a number of technical issues that need to be addressed before the technique finds more widespread use:

1. The classical multiple scattering theory used to interpret ultrasonic measurements gives excellent agreement with experimental data for semi-dilute emulsions containing noninteracting droplets. Nevertheless, it needs to be extended so that it can be applied to more concentrated emulsions and to take into account the effects of droplet flocculation.

2. The interpretation of ultrasonic measurements requires knowledge of a number of the thermophysical properties of the disperse and continuous phases, which are often not readily available in the literature or are difficult to measure. It is therefore important to develop a database of the relevant thermophysical properties for the materials commonly found in colloidal suspensions.

3. The presence of small gas bubbles can obscure the signal from colloidal particles because of their ability to strongly scatter ultrasound. Strategies for overcoming this problem need to be developed, e.g. degassing the sample or making measurements at frequencies where the gas bubbles do not scatter significantly.

ABBREVIATIONS AND ACRONYMS

FT   Fourier Transform
UAS   Ultrasonic Attenuation Spectroscopy
UVS   Ultrasonic Velocity Spectroscopy

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