Ultrasound Based Process Monitoring Using Advanced Data Processing and Analysis
A. Shukla, A. Prakash* and S. Rohani
Department of Chemical and Biochemical Engineering
University of Western Ontario, London, Ontario N6A 5B9 CANADA

Abstract
The inherent ability of ultrasound to penetrate dense and optically opaque suspensions along with its fast response time makes it a desirable technique for online monitoring of industrial processes. A method based on ultrasonic attenuation spectroscopy for monitoring particle size distribution variations in dense and opaque suspensions is presented. Advances in the hardware required for ultrasound signal generation, maintaining signal stability and higher signal to noise ratio has provided the ability to accurately measure the attenuation spectra over a wide range of frequencies. Potential applications include online monitoring of nucleation /crystallization in pharmaceutical /food and mineral processing. In these processes it is essential to monitor changes in particle size to ensure product quality, conformity and to avoid complications in down stream processing by maintaining desirable operating conditions.

Although ultrasonic based methods suitable for dense suspensions of colloids and emulsions have been developed, their applicability in systems with larger particle size is limited due to unavailability of a reliable theoretical model for large particle/crystal sizes. Like many other techniques the accuracy of a deconvolution algorithm to determine particle size is limited by the adequacy of the underlying theoretical model. This study discusses a novel approach for predicting ultrasonic attenuation in the intermediate regime of wave propagation and an optimized deconvolution algorithm for signal processing and extraction of particle size information. The technique has been extensively tested in concentrated suspensions of inert particles. The performance has been further tested and validated with offline laser diffraction measurements for the crystallization of a model pharmaceutical compound. The novel technique will enable the development of an ultrasonic attenuation spectroscopy based online particle sizer capable of operating in concentrated suspensions (up to 30 vol.%) over a wide particle size range (1-1000μm).

Keywords: Ultrasonic; Attenuation Spectroscopy; Particle Size Analysis; Dense Suspensions; Online Monitoring; Advanced Data Processing

Introduction
The properties, handling and processing of powders are affected by the particle size distribution. Various techniques have been developed for the measurement of particle size. These can be classified under particle counting, fractionation and macroscopic techniques. Particle counting techniques generate number weighted size distributions and include electrozone/optical counters and optical/electron image analysis. Particle counting techniques generate a full size distribution as individual particles are counted. Full particle size distributions can also be obtained by fractionation techniques which rely on the separation of particles in different size fractions. These techniques include sedimentation and sieve analysis. Macroscopic techniques utilize the measurement of changes in physical phenomena (light or sound) which are affected by the presence of particles. These techniques relate the changes in the measured quantity with particle size using theoretical formulations. Depending on the measurement principle, different characteristics of the particles are measured and hence different measures of size are obtained. For example the sieve diameter is the width of the minimum square aperture through which a spherical particle will pass whereas the Stokes diameter is the diameter of a free falling sphere. However, particles encountered in most industrial applications have an irregular shape and can not be described using a single geometrical parameter such as diameter. The size of these particles is generally expressed in terms of statistical diameters or equivalent spherical diameters (ESD). Statistical diameters (e.g. Feret’s or Martin’s) describe the mean value of sizes measured along different directions on the projected particle outline. The ESD is the diameter of a sphere that causes the same change in measured property as the particle. For example the Stokes diameter is equivalent to the size of a free falling spherical particle.

Equivalent spherical diameter shows a functional variation with shape depending on the method of measurement. Due to this reason, the ESD obtained using different techniques are not the same. However, it is possible for particle of different shapes to have the same ESD when measured using a particular technique. Hence, it is useful to define shape factors such as aspect ratio and sphericity to obtain a correlation between measured ESD and shape of the particles. Existing measurement techniques only predict the size distribution based on spherical equivalent diameter and assume that the particle shape is homogenous. Some studies [1] have tried to determine the shape factors by making measurements using various techniques and comparing them to estimate the aspect ratio.

Generally particulate systems in industrial processes are polydispersed in nature and consist of a distribution of different sizes occurring at specific frequencies. These systems are defined by the average and width of the distribution. The distribution average is a measure of its central tendency and includes the mode, median and mean. Mode is the most frequently occurring value in the distribution whereas median divides the distribution in to two equal parts and the mean value is the center of gravity of the distribution. The width of a distribution is defined by the standard deviation and is calculated with respect to the central tendency used to describe the distribution average.
There are various analytical distributions which can be used to define a particle size distribution (PSD) using mathematical expressions. Log-normal distribution is the most frequently occurring distribution in particulate systems and is used extensively for PSD measurements. Particle sizing techniques compare the measured size dependent physical phenomenon with theoretically computed values using different distribution parameters to obtain the best fit.

Particulate operations are dynamic in nature and the change in size distribution could be due to particle growth, attrition and/or agglomeration. Down-stream processing and end product quality in these systems can be significantly influenced by the particle size distribution. For example, changes in PSD during crystallization due to product classification can lead to open loop unstable behavior. A real-time knowledge of the PSD in these systems is essential for implementation of control algorithms to obtain desired end product quality. However, online size measurement is only possible with in-situ techniques. Hence, particle sizing techniques based on sieve analysis, sedimentation and optical/electron microscopy are inherently unsuitable for online applications due to the long delay-time associated with sample preparation/measurement. Sampling itself can lead to errors if it is inadequate or unrepresentative.

**Background- Particle Sizing Techniques**

Online determination of particle size distribution requires in-situ measurements. The techniques capable of in-situ measurements include laser diffraction, laser reflectance and ultrasonic attenuation spectroscopy. These techniques are based on different measurement principles and hence give a different measure of PSD. Laser reflectance measures the number based chord length distribution whereas light scattering and ultrasonic spectroscopy generate volume-based distributions.

<table>
<thead>
<tr>
<th>Laser Forward Scattering</th>
<th>Laser Reflectance Method</th>
<th>Ultrasound Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement Principle</td>
<td>Forwards scattered light</td>
<td>Back scattered light</td>
</tr>
<tr>
<td>Transparency Required</td>
<td>Required</td>
<td>Required</td>
</tr>
<tr>
<td>Nature of PSD</td>
<td>Volume weighted PSD</td>
<td>Unweighted chord</td>
</tr>
<tr>
<td>Penetration depth</td>
<td>4mm, for&lt;1 vol. %</td>
<td>Only at probe surface</td>
</tr>
<tr>
<td>Concentration</td>
<td>Dilute</td>
<td>Dense</td>
</tr>
<tr>
<td>Size range (Projected)</td>
<td>0.5 to 1000 µm</td>
<td>0.5 to 2000 µm</td>
</tr>
<tr>
<td>Application</td>
<td>Mainly off-line</td>
<td>In-situ</td>
</tr>
</tbody>
</table>

Recent advances have also been made in online microscopic image analysis. Although particle shape information will be more readily available using this technique it is not suitable for online PSD measurements. On-line microscopic analysis is not considered for further discussions here as this is a particle counting technique. A large number of particles have to be considered to obtain a reliable size distribution using this technique and suspension transparency is essential.

**Laser Diffraction**

Laser Diffraction is one of the most widely used techniques for determining particle size distribution. This technique is based on the principle of forward scattering of a broad laser beam passing through a suspension of particles. A Fourier lens is used to focus the forward scattered light on to an array of photo-detectors perpendicular to the laser source. Scattering may be caused due to diffraction at the particle edges, refraction of light passing through the particles and reflection from the external or internal surfaces. For larger particles (>4-µm) the Fraunhofer theory can be used as diffraction is the dominant scattering phenomenon whereas the Rayleigh theory is applicable to particles in the sub-micron region [2]. Most modern particle size analyzers based on this technique use the Mie theory as it can account for different types of scattering. The variation in scattered light intensity as a function of the scattering angle (θ) and particle size can be calculated using Equation 1 [3].
\[ I(\vartheta) = L_0 \int_{0}^{\infty} f(r) \left( \frac{r J_I(\vartheta, r)}{J_0(\vartheta)} \right)^2 \, dr \]  

where, \( \alpha_{ld} = \frac{2\pi \lambda}{r} \)

Particle size analyzers using laser diffraction assume a spherical particle shape and absence of multiple scattering. However, most industrial systems operate at high concentrations where this technique becomes inapplicable due to its limited penetration depth and multiple scattering. In such systems the measurements are made by continuously circulating the particles through a measurement cell after automatic slurry dilution.

Reproducibility of size measurement using laser diffraction depends on the accuracy of detector alignment with laser source. Misalignment was found to severely affect PSD measurements in simulated studies reported by Wang and Shen [4] for mono-sized particles. Various algorithms are available for deconvoluting particle size distribution and have been reviewed by [3]. However, Etzler and Deanne [5], Neumann and Kramer [6] and Pei et al. [7] have shown that the choice of deconvolution algorithm can effect the PSD.

The major drawback of laser diffraction technique is its inability to make in-situ measurement in dense suspensions. In-line mode of operation is essentially automatic slurry sampling as dilution is still needed to obtain the PSD. Slurry dilution also leads to error and increase in operating time as multiple measurements have to be made for obtaining a representative size distribution. Transport of slurry through a recirculation loop can also lead to changes in PSD due to particle breakage. Furthermore, design modification of the process itself is required to accommodate the re-circulation loop for in-line measurements.

**Laser Reflectance**

The focused beam reflectance method (FBRM) can be used for in-situ measurements in dense suspensions and is being rapidly adopted as a method of detecting particle growth and attrition in a number of industries. This technique is based on laser back reflectance and measures the chord length distribution of particles. Implementation of FBRM is done using a cylindrical probe [8], in which a laser beam with a wavelength of 780nm is rotated at high velocity (~4500rpm). This beam enters the suspension through a sapphire window at the probe tip and can be focused at various depths in the suspension. Particles crossing the focal point reflect the laser beam back into the probe where they are detected by optical sensors. These sensors convert the light energy into electrical signals which are passed through a discriminator circuit to filter signals with long rise times [9]. This helps in the elimination of signals generated from back reflection of particles at positions other than the focal point. The product of measured crossing time (of particle) and the beam velocity are used to calculate the chord length. These chord lengths are added to obtain finite number of chord length intervals or channels.

The FBRM technique measures thousands of chord lengths per second and gives an unweighted chord length distribution (CLD). Since the laser beam randomly scans the particle surface, it measures the chord lengths corresponding to the projected area of the particles. Various studies have been conducted to evaluate the effect of operating parameters such as solids concentration and focal point position on the measurement of CLD in suspensions. Heath et al. [8] have shown that the unweighted distributions are sensitive to fine particles with increase in solids concentration. This bias was attributed to the increase in the number of fines scanned by the FBRM probe. The effect of solid-volume fraction on distribution mode was negligible for equivalent spherical size, cube weighted and square weighted chord length distributions [8,10,11]. However, Sparks and Dobbs [10] have shown that laser-lens interactions may cause broadening of the beam due to high solids concentration and solution/particle surface characteristics. This can lead to changes in optimum focal point positions and cause errors in the CLD measurements [12]. Substantial changes were observed in the CLD as a function of focal position and have been investigated by various researchers. Monnier et al. [13] and Law et al. [14] have shown that focal length between 0.8 to 2mm in the solution gave better measurements for larger particles. However, Heath et al. [8] showed that although some improvement may be obtained using a larger focal position for dilute suspensions, the optimal setting for concentrated systems should be zero-microns from the probe window. They reported a drop in chord counts as the focal length was increased away from the probe window. Focal positions very close to the probe window can increase the sensitivity of the unweighted distribution to finer chord lengths as lesser number of larger chords is able to enter the viewing region. This effect can be minimized by using the square-weighted chord length distribution.

A number of studies have tried to correlate the CLD measurements with laser diffraction to obtain a relationship with average particle size [10,13,15]. Heath et al. [8] observed that the mean as well as median were affected by the sensitivity of FBRM measurements to fine particles. However, the mode of square-weighted distribution showed good agreement with the median size obtained using laser diffraction for particles between 20 to 500-\(\mu\)m. Various algorithms have also been developed for converting CLD measurements to size distribution data. Majority of the work dealing with theoretical methods for CLD-PSD conversion assume spherical particles or two-dimensional ellipses. Assumption of a spherical particle size simplifies calculations as orientation effects can be neglected. However, such assumptions are only valid for glass beads or latex suspension and can be considered reasonable in suspensions where the aspect ratio is approximately 1 [8]. Taddayon and Rohani [9] used a two dimensional model approach to obtain PSD from CLD for ellipsoidal and spherical particles. Ruf et al. [16] developed a 3-D model...
of chord length distribution for particles of general shapes. However, they concluded that CLD to PSD inversion is not possible unless the shape of particles is known.

This technique cannot operate in opaque suspensions and the measurements are not representative as they are localized at the probe tip. Particle opacity also has an effect on the measured CLD and transparent particles cannot be properly sized due to poor reflectivity [10]. FBRM measurements are susceptible to particle shadowing (due to the presence of fines), particle masking (due to coarse particles) and the assumption that the entire particle projection area has perfect back reflectance. Furthermore, CLD measurements are significantly affected by particle shape and can lead to large errors in PSD deconvolution unless the shape is known beforehand.

**Ultrasonic Spectroscopy**

Ultrasonic techniques can be used for online measurement of volume-weighted particle size distribution in dense and opaque systems. This technique is based on the propagation of an acoustic pulse through the suspension and measures the change in its attenuation and acoustic velocity caused by the presence of particles (Figure 1). The ability of this technique to penetrate dense suspensions are shown in Figure 2 [17]. The settling characteristic of 43 and 168-μm mixed particle system was monitored using ultrasonic velocity. The measurements were made in through transmission mode with transducer separation of 25mm. It can be seen from the figure that segregation could be easily measured using ultrasound and the trends closely correspond to the theoretical model of Schneider et al. [18]. The measurements were also able to pick up concentration and size gradients.

The changes in the parameters of the acoustic pulse show frequency dependence with respect to particle size. Attenuation and velocity in suspensions are also affected by the properties of the liquid phase and the frequency dependence of these parameters becomes more pronounced with increasing viscosity and molecular scale relaxations in the liquid (e.g. oily liquids). However, irrespective of the liquid phase the presence of solids causes a substantial change in attenuation as compared to acoustic velocity measurements. Hence, majority of the ultrasonic techniques utilize attenuation spectrum measurements over velocity spectrum for particle sizing.

Loss of energy contained in the acoustic pulse can be due to different attenuation mechanism. These attenuation mechanisms can be classified under absorption and scattering losses. The dominant loss mechanism is dependent on the regime of wave propagation which is classified using a dimensionless parameter called the wavenumber ‘kr’. The wavenumber is calculated using the particle radius ‘r’ and ultrasonic wavelength ‘λ’. The various propagation regimes based on ‘kr’ are summarized in Table 2 along with the prevalent attenuation mechanism.

**Table 2. Ultrasonic Propagation Regimes.**

<table>
<thead>
<tr>
<th>Wavenumber (kr=2πr/λ)</th>
<th>Regime of Propagation</th>
<th>Loss Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>kr&lt;&lt;1</td>
<td>Long wave regime</td>
<td>Absorption losses are dominant</td>
</tr>
<tr>
<td>kr~1</td>
<td>Intermediate regime</td>
<td>Scattering losses are dominant</td>
</tr>
<tr>
<td>kr&gt;&gt;1</td>
<td>Short wave regime</td>
<td>Geometrical scattering</td>
</tr>
</tbody>
</table>

Ultrasonic measurements in the long and intermediate wave regime are sufficient for obtaining PSD measurements for industrial processes as these can cover particles from the sub-micron to the micron region. Similar to other techniques ultrasonic attenuation spectroscopy optimizes the parameters of assumed distribution by minimizing the error between predicted and measured attenuation spectrum. Theoretical models available for attenuation predictions in dense suspensions are only applicable in the long wave regime. Hence this technique is limited to particles smaller than 100-μm. In this regime the absorption losses are dominant and the effect of scattering is insignificant. Absorption losses are hydrodynamic or thermodynamic in nature and are caused by the interaction of particles with the pressure field generated by the acoustic pulse.

The most widely used ultrasonic attenuation model was initially developed by Epstein and Carhart in 1941 for sound propagation in air with suspended fog droplets. Allegra and Hawley [19] modified this model for applications in colloidal suspensions and developed explicit equations for attenuation calculation. The ECAH (Epstein-Carhart and Allegra-Hawley) theory calculates the attenuation for a single particle and the total attenuation is obtained by superposition of the contributions of each particle. Under dilute conditions (<10 vol. %) the superposition theory is valid as particle-particle distance is sufficient to avoid the overlap of the viscous layers of individual particles. Gibson and Toksoz [20] developed a coupled phase model to account for the effects of viscous length overlap for mono-sized particles. Dukhin and Goetz [21] generalized the coupled phase model for poly-dispersed suspensions.

The major limitation of ultrasonic techniques is its inability to size larger particles due to the unavailability of theoretical models to predict scattering. Scattering is caused by the redirection of the energy contained in an acoustic pulse by the particles and is dominant when the wavelength is comparable to the particle size. Various attempts have been made to develop a scattering theory applicable at higher wave numbers [22,23,24,25,26]. However, these models did not show good agreement with measurements in dense suspensions.

In the absence of a reliable scattering model efforts were made using empirical models to obtain the relationship...
between particle size and measured attenuation. This technique is based on the measurement of particle size fractions using offline techniques such as laser diffraction. The attenuation spectrum of these particles was then measured and calibration equations were generated to obtain the frequency response of different size fractions. This technique can be used for a broad range of particle sizes but requires customized calibration for specific applications. Furthermore, changes in particle shape and/or size, fluid properties (e.g. density or compressibility) can lead to significant errors as the calibration model does not account for them. Hence, theoretical scattering models applicable in dense suspensions are desirable to extend the use of ultrasonic techniques for larger particles.

**Novel Ultrasonic Technique- Results**

Morse and Ingard [27] model, has the capability of operating in the intermediate regime of wave propagation. Equations 2 and 3 show the explicit equation for calculating the scattering and absorption cross sections using this model.

\[
\Sigma_s = \frac{4\pi}{k^2} \sum_{m=0}^{\infty} \left(2m+1\right) j_m^2(kr) + i \beta_m j_m(kr)
\]

\[
\Sigma_a = \frac{k^4r^4}{4\pi^2} \sum_{m=0}^{\infty} \left| j_m^2(kr) + i \beta_m h_m(kr) \right|^2
\]

A comparison with experimental results has shown that the model performance is extremely good at low concentrations (<2 vol.%) [28]. However the model tends to significantly deviate with increase in particle concentration. The deviations in this and other intermediate regime models have often been attributed to particle-particle interactions. However, Dukhin and Goetz [21] have experimentally shown that multiple scattering effects are minimal up to 40 vol.% concentration.

Shukla et al. [28,29] have shown that the model [27] non-performance in dense suspensions can be attributed to directional scattering. The original Morse and Ingard [27] model does not account for the finite sensor size and geometry. Model modification incorporating these effects leads to significant improvements in dense suspension attenuation predictions. The novel model along with an optimized deconvolution algorithm [28,30,31] has resulted in the measurement of PSD in dense suspensions of particles lying in the intermediate propagation regime.

Figure 3 shows the PSD measured using ultrasonic attenuation spectroscopy technique at 12 vol.% for 43 and 202-µm glass particles [28,29]. Offline PSD measured using Malvern Mastersizer ® at concentrations less than 1 vol.% are also shown in the figure and is similar to the measurements obtained using the ultrasonic technique at higher concentrations. Figure 4 shows the online measured PSDs [30] using ultrasonic techniques during crystallization of a model pharmaceutical compound. A comparison with offline PSD measured using Malvern Mastersizer ® for a sample retrieved at the end of crystallization shows good agreement with the ultrasonic spectroscopic results.

**Conclusions**

Various particle size measurement techniques were compared with respect to their suitability for in-situ measurements. Laser diffraction technique can not operate in opaque and dense systems due to limited light penetration. This necessitates the use of in-line measurements to accommodate slurry dilution. However, this mode of measurement is not truly online due to the time-delay associated with slurry circulation and dilution. The removal of slurry from the process and dilution can also cause changes in the nature of the PSD. Unlike laser diffraction, FBRM measurements are capable of making in-situ measurements and hence can be used for online applications. However, this technique cannot be used for opaque suspensions and the measurements are non-representative as measurements are limited to the particles present at the probe surface. Ultrasonic techniques can overcome the limitations of light-based measurements as it can operate in opaque suspensions and has good penetration depth (>25mm) even under dense conditions. The measurements obtained using this technique is more representative when compared to laser diffraction as well as laser reflectance techniques. The current application of this technique was limited to particles smaller than 100-µm due to the unavailability of theoretical models for dense suspensions of large particles. These drawbacks have been overcome by the modified intermediate regime model proposed by Shukla et al. [28,30,31] and has the potential for online particle sizing in industrial applications.

**Nomenclature**

- \( h_m, h'_m \): Hankel function and its derivative
- \( I, I_0 \): Final intensity (W.m\(^{-2}\))
- \( j_m, j'_m \): Bessel function and its derivative
- \( kr \): Non-dimensional wavenumber (-)
- \( m \): Integer (-)
- \( r \): Particle radius (m)

**Greek Symbols**

- \( \beta_m \): Surface Admittance (-)
- \( \lambda \): Wavelength (m\(^{-1}\))
- \( \vartheta \): Scattering angle (rad)
- \( \Sigma_a \): Absorption c/s area (m\(^{-2}\))
- \( \Sigma_s \): Scattering c/s area (m\(^{-2}\))

Shukla et al. Page - 5
Author Bio

Dr. Abhishek Shukla is a post doctoral fellow in the Department of Chemical and Biochemical Engineering at the University of Western Ontario (UWO).
Email- ashukla3@uwo.ca

Dr. Anand Prakash is a Professor in the Department of Chemical and Biochemical Engineering at UWO. He is a Steering Committee member of the Particle Technology Research Center (PTRC) at UWO.
Email- aprakas2@uwo.ca

Dr. Sohrab Rohani is a Professor in the Department of Chemical and Biochemical Engineering at UWO. He is a Director of PTRC and founder of Crystallization and Control of Pharmaceuticals Laboratory (CCPL) at UWO.
Email- srohani@eng.uwo.ca

Literature Cited


[28] A. Shukla, Ultrasonic Techniques for Dispersed Phase Characterization., Department of Chemical and Biochemical Engineering, University of Western Ontario (Ph.D.), London, Ontario, 2007.


Figure 1. Propagation of longitudinal ultrasonic waves in suspensions.

Figure 2. Simulation of bi-disperse suspension (43 and 168-μm) using Schnieder et al.
[18] model and comparison with change in acoustic velocity measurements [17].
Figure 3. Comparison of PSDs (43 and 202-μm) [29] measured using the novel ultrasonic attenuation spectroscopy technique [28, 29, 31] at 12 vol.% with offline laser diffraction (<1 vol.%) results (Malvern Mastersize ®) for glassbeads suspended in water.

Figure 4. Online measurements of PSD [30] using Shukla et al. technique [28, 29, 31] at various times during crystallization. The offline measurement from Malvern Mastersizer ® is shown for comparison with the online ultrasonic PSD at the sample retrieval time.