

Ultrasonic Pulsed Doppler, a Novel Method for Nanoparticle Characterization

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ABSTRACT

USPD is a unique ultrasonic backscatter technology for the characterization of nanoparticles. Particles are interrogated in motion and the backscattered energy is received at Doppler-shifted frequencies, allowing clutter-free detection of backscatter from particles in the sub-ten to 100 nm range. For sizing, particles are set into motion by high intensity interrogation ultrasound itself with velocities correlated with size and the backscatter power spectrum is converted to a Particle Size Distribution (PSD). This process is less labor intensive and expensive than TEM and has advantages over legacy optical methods. Employing only a single small transducer, USPD systems can be incorporated into existing process equipment. Other advantages include measurement at high concentrations and with opaque solutions and better size resolution than with many conventional instruments. USPD can also measure concentration and flow fields with high spatial resolution.

Keywords: particle characterization, particle size distribution, ultrasonic backscatter

1 INTRODUCTION

Ultrasonic Pulsed Doppler (USPD) is a unique particle characterization system based on measurement of Doppler shifted ultrasonic backscatter from moving particles. Due to their small size, backscatter from nanoparticles is weak and conventional wisdom holds that it cannot be harnessed as a practical measurement method. However, by shifting the signal to a frequency differing from that of the interrogating signal, clutter is not an issue and a very large measurement dynamic range is achieved. This supports a measurement system requiring only a single small transducer that can be part of a dedicated instrument or used in-situ, e.g., inserted into existing equipment. Measurement of concentration, high-spatial resolution flow velocity and particle size distribution are made with very simple analysis algorithms.

2 THE USPD SYSTEM

Principles of Operation

Rayleigh Scattering In the long wavelength limit $a \ll \lambda$, where a and λ are the radius of a particle and the wavelength of the ultrasound, the backscatter of an interrogating plane wave of amplitude p_i to a scattered spherical wave of amplitude $p_s(r)$, at a distance r from the transducer follows Rayleigh scattering, to wit:

$$\Phi = \frac{r p_s(r)}{p_i(r)} = \frac{1}{3} k_0^2 a^3 \left[\frac{\kappa_1 - \kappa_0}{\kappa_0} - \frac{3(\rho_1 - \rho_0)}{2\rho_1 + \rho_0} \right]$$

Here k_0 is the wavenumber of the interrogating sound, ρ_1 and ρ_0 are the densities of the particle and the suspending medium and κ_1 and κ_0 are the corresponding compressibilities. The term in front of the brackets defines the frequency dependence and is also proportional to a^3 , which when converted to power is an a^6 dependence. This term is extremely small for nanoparticles at Mhz frequencies. For example for 16 Mhz with $a = 10$ nm and $r = 5$ mm, the term $k^2 a^3 / r$ is on the order of 10^{-12} , illustrating the weakness of the scattering. The quantity in brackets describes the contrasts between the physical properties of the particles and the suspending medium. The first term describes monopole scattering due to particle radial oscillations driven by the compressibility contrast and the second term describes dipole scattering due to oscillatory particle motion driven by the density difference. The scattered power from a random distribution of particles N per unit volume is assumed to be proportional to $N\Phi^2$.

Particle Velocity and Doppler Shift USPD collects scattered ultrasonic energy from particles in motion. For backscatter, the scattered wave experiences additive negative Doppler shifts on excitation and re-radiation so that for a velocity v away from the exciting transducer the Doppler shift at frequency f of the received signal is $\Delta f / f = -2v/c$ where c is the velocity of sound in the medium. In most USPD

applications, velocities are on the order of cm/sec giving rise to Doppler shifts of hundreds of Hz. Particle motion can be created in several ways:

1. Intrinsic: Particles are part of an existing stream, such as in a manufacturing process.
2. Extrinsic: Samples are stirred in a test volume. Concentration is typically measured with stirred solutions.
3. Excitation by Interrogating Signal: Here unidirectional particle motion is created by the interrogating signal itself. This occurs when a strong signal creates forces on the particles and/or the medium which can be set into bulk motion by streaming. This configuration enables particle size measurement.

Configuration: Figure 1 sketches two generic USPD configurations. On the left, a focused transducer is inserted into a vessel containing a suspension of particles. In much of our research the most common laboratory configuration has been a small plastic cylindrical chamber containing 1 ml of fluid. Driven by a signal generator, the transducer typically broadcasts a series of 50 cycle 16 Mhz tone bursts with a gap between them during which backscattered energy enters the transducer. The interrogating field is tightly focused down to a very small focal volume in order to achieve the high levels of intensity necessary to generate the required particle velocities. On the right is a sketch of a geometry in which the focal zone is within an existing flow and the transducer is positioned outside and looks through an acoustic window so that it is not in direct contact with the flow. Backscatter is measured from the particles passing through the focal zone indicated in red.

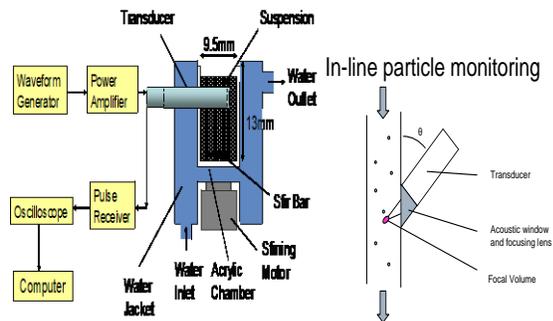


Figure 1: Left, laboratory batch arrangement; Right, application of USPD to existing stream.

Signal Processing The basic unit of USPD processing is the power spectrum of the backscatter. As presently configured, a 40 ms time series is collected consisting of an attenuated version of the incident signal and an amplified version of the backscatter falling between the tone bursts. Power spectra of this signal are generated with 25 Hz bin widths using a Teledyne LeCroy 12-bit oscilloscope and several spectra are averaged. These average power spectra include bleed-through of the incident signal as a “main peak” and Doppler-shifted backscattered power appearing to the left of this peak when the particles are moving away from the transducer. In the concentration measurement configuration the sample is stirred and turbulent velocities create Doppler shifted backscatter on both sides of this main peak. The distribution of values of spectral power in each bin is compared to that found in spectra taken with very pure water to identify and isolate the contributions of backscattered energy in each frequency bin. An example of a spectrum taken with nominal 50 nm gold particles is shown in Figure 2. The blue curve represents the average spectrum and the red curve is the “distribution filtered” version which differs from the original by recording power only in those bins in which backscattered energy is detected. The main peak is at bin 106 and there are two other peaks at bins 78 and 90 representing Doppler shifts of 384 and 672 Hz, indicative of a mixture of two induced velocities and two particle sizes.

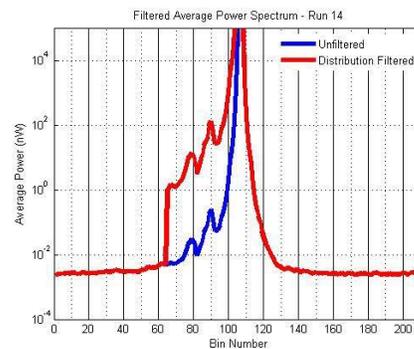


Figure 2: Power spectrum of backscattered energy from nominal 50 nm gold particles consisting of main peak at bin 106 representing the interrogating signal and two peaks to the left indicating two particle sizes.

3 NANOPARTICLE SIZING

Particle size measurements are based on the previously unknown phenomenon that under high levels of ultrasonic excitation nanoparticles are accelerated to velocities that are uniquely correlated to their size due to the combined effects of size-dependent ultrasonic and drag forces. PSD's are generated by conversion of backscatter spectra Doppler shifted components to

size using known relationships between and size and velocity. These “calibration curves” have been developed for polystyrene and silica particles in the 10 – 100 nm range. Work is ongoing to improve the accuracy of these curves and to develop similar ones for higher density particles (e.g. silver and gold). As the analysis makes no *a priori* assumptions about the shape of the particle size distribution, the resolution can be greater than that obtained by, e.g., DLS.

Calibration Curves

Calibration curves relating Doppler shift (in terms of 25 Hz wide bins away from the main peak) to size are developed by comparing USPD spectra to TEM-derived PSD’s for the same samples. Curves for polystyrene (data from 2011) and silica (2013) are shown in Figure 3. Curves fitted for the two particle types and for all the data are shown. The Doppler shifts increase more rapidly as particle size decreases and the fitted curves are similar to a 1/diameter relationship. Both types of particle follow similar relationships. However, there is no *a priori* reason to expect that there is a universal curve applicable to all types of particles.

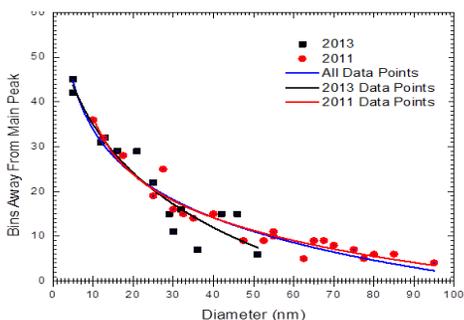


Figure 3: Calibration curves for polystyrene and silica nanoparticles.

Particle Size Distribution Example

USPD particle size distributions are constructed by converting backscatter spectra containing Doppler shifted power to diameter using a calibration curve and displaying size information as a histogram with bins of equal particle diameter width. As an example, consider a commercial suspension of polystyrene particles purported to be monodisperse at 96 nm. A TEM image of this suspension in Figure 4 shows that there are two populations roughly around 20 nm (lighter color) and larger particles in a range around 60 nm (darker color). Note the size bar in the lower right that is 50 nm.

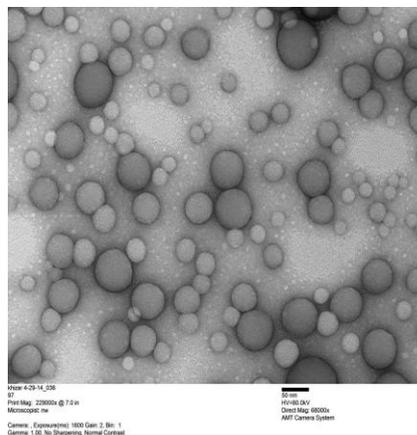


Figure 4: TEM image of purported 96 nm monodisperse polystyrene

An Image J generated PSD based on TEM images in Figure 5(a) has a dominant population peaking around 22 nm and smaller numbers from about 40 to 100 nm, with a general peak centered around 60 nm. By comparison, the USPD PSD in Figure 5(b) indicates a main population peaking between 25 - 30 nm and a second population between 45 and 90 nm that is more pronounced than what is recorded by TEM. While USPD indicates a main population at slightly larger size than that indicated by TEM and a greater relative number of larger particles, there is good qualitative agreement with TEM. (Actually, the qualitative impression given by the TEM image suggests that the TEM PSD may underestimate the number of larger particles.) Efforts to improve the accuracy of all aspects of USPD are ongoing.

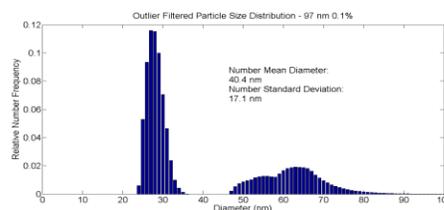
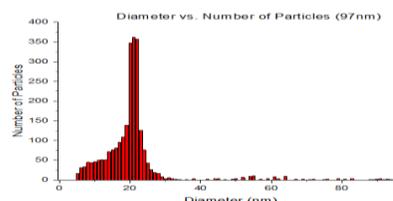


Figure 5: (a) TEM for nominal 96 nm PS particles; (b) USPD PSD at 1% wt/wt concentration; (c) USPD PSD at 0.1% concentration.

4 HIGH RESOLUTION VELOCIMETRY

USPD can also measure velocities in existing flows without contact with the fluid. A configuration with milk flowing through an elbow is shown in Figure 6. Here the transducer is mounted entirely outside the flow and “looks into” it through a thin elastomeric sheet acting as an acoustic window. In this configuration the transducer focal volume is in the flow on the other side of the window, and the backscatter propagates from it back through the window to the transducer.

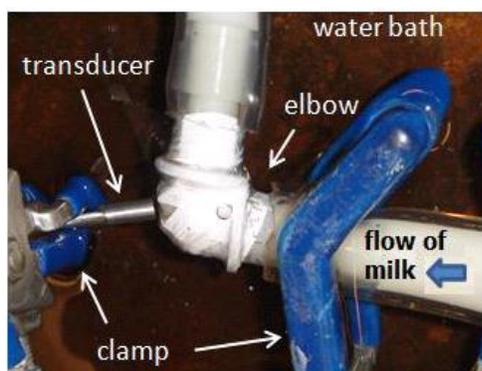


Figure 6 Monitoring of milk flow through elbow

USPD spectra for several flow speeds measured with the flow reversed from this configuration and with the flow direction as shown (toward the transducer) are shown in Figures 7 and 8. Consider first Figure 7 showing the backsacter spectra for flow in the direction opposite to that shown in figure 6. Obvious Doppler-shifted peaks appear on the left side of the main peak indicating bulk flows moving away from the transducer with indicated speeds corresponding to independently measured values. The spectra for flow toward the transducer in Figure 8 are completely different. Here there are large contributions close to and on either side of the main peak indicating flows in both directions with speeds from about -5 to +14 cm/sec. Spectral components due to the main flows to the right of the main peak are almost indistinguishable. The former represents turbulent secondary flows both toward and away from the transducer. These are secondary flows probably generated by interaction with the transducer, residing in the focal volume in this geometry. With oppsite bulk flow, secondary flows, if present, do not exist in the focal volume and are not present in the backscatter spectra. This illustrates the potential for high spatial resolution

velocimetry and the potential for incorporation into existing equipment.

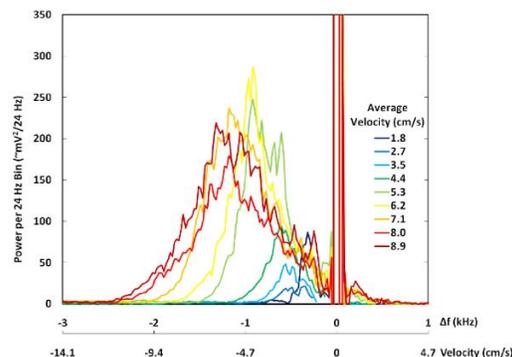


Figure7: Backscatter Spectra for flow in opposite direction

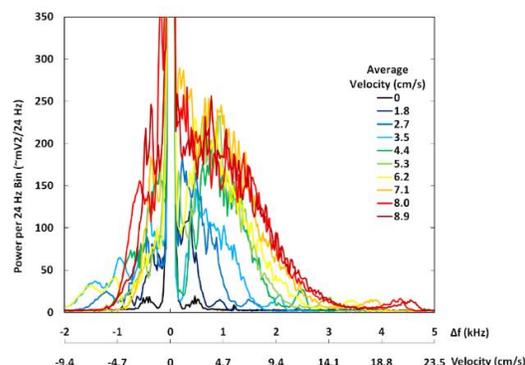


Figure8: Backscatter spectrum with flow toward the transducer

5 SUMMARY ADVANTAGES OF USPD

USPD is a unique particle characterization system. It can measure particle size distribution at much lower cost and effort than TEM, with better resolution than other methods and not requiring complex mathematics typical of other ultrasonic methods. As it uses only a single transducer that probes a small focal volume. In addition, it can be incorporated into existing equipment to monitor particle characteristics during processes (e.g PAT) or flow rates. It can be used with opaque suspensions without dilution. Contact with the suspension being sampled is not required when an acoustic window can be used. Also, in addition to be able to measure concentration by computing total energy backscattered (not illustrated here), and, as ultrasonic backscatter is a function of particle material properties including compressibility as described by Raleigh scattering, it may be able to measure and/or monitor particle density and/or compressibility or changes to these properties with time during a process.