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Characterisation of colloidal dispersions using ultrasound spectroscopy and multiple-scattering theory inclusive of shear-wave effects

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ABSTRACT

Ultrasonic spectrometry measures the attenuation of a sound wave propagating through a sample. In slurries the ultrasound signal becomes highly attenuated as a function of particle size, concentration and density. To monitor these properties in slurries the attenuation requires interpretation using a mathematical model. We examine different sizes of silica suspended in water, at different concentrations, and frequencies up to 100 MHz. We determine that a new multiple scattering theory inclusive of shear-wave reconversion effects (i.e. conversion of compressional wave to shear wave and back to compressional wave at the particle/liquid boundary) is successful for attenuation prediction in the range up to ≈20 MHz and 20% (by volume). Beyond this level the model with shear-effects begins to deviate from the real attenuation, but is still more representative of the experimental results than modelling only an incident compressional wave. Thus, shear-wave reconversion modelling is essential to more accurately reflect the attenuation spectra in a solid particle in suspension system, and dictates the ultrasonic attenuation as particle sizes decrease and concentration increases.

1. Introduction

Ultrasonic spectroscopy, coupled with an appropriate algorithm to determine particle characteristics in suspension, has the potential to become the modality of choice for process monitoring in next-generation nanofluid and colloidal processes. Many such complex fluids are optically opaque, precluding the use of optical analysis techniques without sample modification such as dilution. Industrially, for example, it is impractical to analyse a slurry using photon correlation spectroscopy since the particle suspension has to be diluted to very low concentration in order for the size distributions of the suspended medium to be determined. Ultrasonic techniques are not hindered by opacity, can be used without sample modification, and lend themselves to in-line applications (Challis et al., 2005; Ouriev et al., 2003). Shukla et al. (2007) used an ultrasonic technique to study sedimentation processes which occur in fluidised beds, separators and hydraulic conveying, as well as for particle sizing (Shukla et al., 2010). Conversely, the creaming instability of food emulsions was investigated by Povey's group (Dickinson et al., 1994). A number of workers have applied ultrasonic techniques to the monitoring of crystallisation processes (Hipp et al., 2000; Shukla et al., 2010; Mougin et al., 2003; Frohberg and Ulrich, 2015) which are of relevance in the food and pharmaceutical sectors amongst others. A variety of other applications

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have been investigated by ultrasound, including monitoring particle size reduction for process intensification (Ruscitti et al., 2008), aggregation in petroleum (Abbott and Povey, 2012), emulsion polymerisation (Pawelzyk et al., 2013) and monitoring of concentrated slurries (Stolojanu and Prakash, 2001). Henning and Rautenberg (2006) reviewed ultrasonic process monitoring systems in 2006. The range of these applications illustrates the ubiquity of suspensions of micro or nano-particles in processing applications in a broad range of industries including pharmaceutical (McClements and McClements, 2016), agrochemical (Boyd and Varley, 2001), food (McClements and McClements, 2016; Awad et al., 2012; Chandrapala, 2015; McClements and Gunasekaran, 1997), petrochemical and others where there is a need for reliable and accurate monitoring techniques to guarantee quality and consistency (Hauptmann et al., 2002).

Whilst well-established in the colloidal size range and up to limited particle concentrations, ultrasonic spectroscopy has faced challenges in the nano size range and at higher particle concentrations (slurries) (Challis et al., 2005, 2009; Hipp et al., 2002). These are challenges both of accurate analysis using computationally efficient ultrasonic scattering models and of measurement in highly attenuating concentrated samples (Scott, 2003). We continue to make progress against these challenges here by experimental validation of a new multiple scattering model using two types of ultrasonic spectrometer.

We present comparison of experimental ultrasonic spectra with model predictions for four sizes of silica particles in aqueous suspension. We use a new multiple scattering model inclusive of shear wave reconversion (i.e. conversion of compressional wave to shear wave and back to compressional wave at the interface between a particle and the fluid) and show its necessity for small particles and concentrated samples. We also validate the results obtained with two spectrometers: a legacy Malvern Ultrasizer, and new spectrometer (Digusonic DSX, Challis and Ivchenko, 2011; Phang et al., 2008) designed for in-line monitoring of highly attenuating samples over a frequency range of 1–20 MHz. The developments reported here are key elements in the extension of ultrasonic spectroscopy to the nano-particle size range and to highly concentrated systems, permitting the technique to deliver its potential for particle characterisation and process monitoring in these significant regimes.

2. Multiple scattering model with shear wave reconversion

Our objective is to show that the inclusion of shear-wave reconversion phenomena in the modelling of suspensions of solid particles in ultrasonic fields is necessary and becomes non-negligible as particle size decreases and concentration levels increase. The mathematical details of a new model of multiple scattering that includes both thermal and viscous effects was given in 2012 by Luppé/Conoir/Norris (*LCN*) (Luppé et al., 2012), from which we outline a reduced form that allows efficient computation of the ultrasonic attenuation (Pinfield and Forrester, 2015; Forrester et al., 2016). From an effective wavenumber the attenuation and speed of sound through a sample can be found (Challis et al., 2005). We define the effective wavenumber as a sum of three parts: that without shear waves, based on the formulation of Lloyd and Berry (*LB*) (Lloyd and Berry, 1967) plus two extra terms due to the shear-mode reconversion (second and third order terms in concentration, respectively). The shear reconversion model (*SM*) is valid in the long wavelength regime whereby the compressional wavelength is much larger than the particle radius. The effective wavenumber takes the form below (Forrester et al., 2016),

$$K_{eff}^2 = \left[K_C^2\right]_{LB} + \Delta_{CS}^{(2)} + \Delta_{CS}^{(3)}. \tag{1}$$

where the second order term is given by

$$\Delta_{CS}^{(2)} = -\frac{27i\phi^2}{(k_C r)^6}\frac{k_C^3 b}{(k_C^2 - k_S^2)}T_1^{SC}T_1^{CS}Y_0 \tag{2}$$

and the third order term is

$$\Delta_{CS}^{(3)} = \frac{3\phi}{(k_C r)^3}\frac{k_C^3 b}{(k_C^2 - k_S^2)}T_1^{SS}Y_0\Delta_{CS}^{(2)} \tag{3}$$

with $Y_0 = k_C b j_0'(k_C b)h_0(k_S b) - k_S b j_0(k_C b)h_0'(k_S b)$. In the above ϕ is the volume fraction; b is the radius of the excluded volume (twice the particle radius, r); k_C and k_S are the fluid compressional and shear wavenumbers, respectively; h_n and j_n are spherical Hankel and Bessel functions; and T_1 are transition factors (scattering coefficients) of partial wave order 1 representing different mode conversions, e.g. *CC* – compressional to compressional, *CS* compressional to shear, etc. The transition factors are (Forrester et al., 2016)

$$T_1^{CC} = i\ \frac{(k_C r)^3\ (\hat{\rho} - 1)\ h_2(k_S r)}{3D(k_S r)} \tag{4}$$

$$T_1^{CS} = -\frac{k_C r\ (\hat{\rho} - 1)}{k_S r\ D(k_S r)} \tag{5}$$

$$T_1^{SC} = -i\ k_S\ k_C^2\ r^3 \frac{2(\hat{\rho} - 1)\ F(k_S r)}{3D(k_S r)} \tag{6}$$

$$T_1^{SS} = \frac{2(\hat{\rho} - 1)\ j_0(k_S r) - 3j_2(k_S r)}{D(k_S r)} \tag{7}$$

where $D(k_S r) = 3h_2(k_S r) - 2(\hat{\rho} - 1)\ h_0(k_S r)$ and $F(k_S r) = h_2(k_S r)\ j_0(k_S r) - h_0(k_S r)\ j_2(k_S r)$. The density ratio of the solid phase (ρ') divided by that of the fluid (ρ) has a strong influence on the system: $\hat{\rho} = \rho'/\rho$. The imaginary part of the effective wavenumber, K_{eff}, allows us to find the attenuation and we compare the results to the experimental values found for four sizes of spherical silica in aqueous media at different concentrations. A full derivation will be provided elsewhere. These equations are entirely driven by frequency, particle size, concentration, density, speed of sound, and viscosity and constitute the shear-mode reconversion model (*SM*).

We extend the analysis over a greater frequency range than we have previously investigated with the current model (Forrester et al., 2016). The values of the densities and particle sizes are found experimentally, as described below, whereas the other physical parameters used in the modelling are to be found in the work of Challis et al as they are standard values given for silica (Challis et al., 2005).

3. Sample preparation and characterisation

During preparation powdered silica was mixed with deionised water (Millipore-Q) in 100 ml batches, slowly stirring it in by hand to produce the initial suspension. Thereafter, each