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Advances in ultrasonic monitoring of oil-in-water emulsions

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ABSTRACT

A modification to the multiple scattering model used to interpret ultrasonic measurements for emulsions is investigated. The new model is based on a development by Luppé, Conoir, and Norris (2012) which accounts for the effects of multiple mode conversions between thermal, shear and compressional modes. The model is here applied to the case of oil in water emulsions in which thermal effects are dominant. The additional contributions are expressed in terms of the scattering coefficients for conversion between compressional and thermal modes and vice versa. These terms are due to the effect of thermal waves produced at one particle being reconverted into the compressional mode at neighboring particles. The effects are demonstrated by numerical simulations for a sunflower oil in water emulsion which show that the additional terms are significant at low frequency and high concentrations. Comparison is also made with experimental data for a hexadecane in water emulsion. Although qualitative agreement is demonstrated, there are some quantitative differences, which are attributed to uncertainties in the physical properties, in the experimental data, or in the assumptions made in the model.

1. Introduction

Low-power non-destructive ultrasonic monitoring techniques have been successfully applied to a variety of hydrocolloid systems. The technique can be used for the measurement of concentration and particle size (Babick, Stintz, & Richter, 2006; Challis, Povey, Mather, & Holmes, 2005; McClements & Coupland, 1996), monitoring instability such as creaming/sedimentation (Pinfield, Povey, & Dickinson, 1996) and flocculation (Chanamai & McClements, 2001; Herrmann, Hemar, Lemarechal, & McClements, 2001), as well as for the detection of structural change such as gelation (Audebrand, Kolb, & Axelos, 2006; Yuno-Ohta & Corredig, 2007) or crystallization (Coupland, 2002). One of the principal formulations for interpreting measurements is that based on a multiple scattering model, treating particles as independent scatterers of ultrasound, and combining the effects of scattering at each particle. Epstein and Carhart (1953) and Allegra and Hawley (1972) derived the solution for the scattering of a sound wave by a single spherical particle, taking into account both the thermal and shear waves produced in the process. Their results, combined with the multiple scattering model of Lloyd and Berry (1967) are here identified as the ECAH/LB model. This model is used to derive the effective wavenumber for ultrasound in emulsions or suspensions, from which the ultrasound speed and attenuation can be determined. The attenuation and speed depend on the physical properties of the component materials, and the particle size distribution (PSD) and concentration. By inverting the model using experimental measurements it is possible to determine PSD, concentration or certain properties by use of the ultrasonic technique. Ultrasonic measurements (of speed or attenuation) are typically carried out in through-transmission mode in the mega-Hertz frequency range which is ideally suited to applications in the colloidal size range. Ultrasonic techniques have some advantages over other process analytical techniques for industrial applications, particularly in the fact that no dilution is necessary, and the equipment can be readily installed in a flow pipe.

The interpretation of measurements is an essential part of the technique, and so the existence of a valid model is crucial. Whilst the ECAH/LB model has been validated and used in a number of applications (see examples in Challis et al., 2005), it is known to break down at low frequencies, high concentrations or small particle sizes. Evidence for the discrepancy between model and experiment can be found, for example in the work of Hipp, Storti, and Morbidelli (2002a, 2002b) for silica in water suspensions and by McClements and others for oil in water emulsions (Chanamai, Herrmann, & McClements, 1999; McClements, Hemar, & Herrmann, 1999). The problem occurs when the thermal and shear waves produced at each particle by the scattering process, propagate a sufficient distance into the continuous phase that they can be re-scattered by a neighboring particle. This can result in a

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"reclaim" of the energy lost in these wave modes, so that the attenuation of the compressional mode (the transmitted mode of propagation) is reduced. The scattering model of ECAH/LB assumed that the thermal and shear wave modes decayed to zero in the space between particles and had no interaction with neighboring particles. This is a reasonable assumption in many cases, since the thermal and shear decay length is of the order of micrometers in water at 1 MHz. The magnitude of the "overlap" effect is governed by both the average interparticle distance, and the decay length of the thermal and shear wave modes (proportional to their wavelength). The effect becomes stronger at lower frequencies (where the decay length is longer), smaller particle size (where the interparticle distance is reduced at the same volume fraction of particles) and at higher concentrations (where the interparticle distance is reduced). Fig. 1 illustrates the scattered compressional and thermal modes, which contribute to the wave field which is incident at a neighboring particle.

The thermo-elastic effect which relates to the *thermal* scattering problem was solved by Isakovich (1948) for dilute emulsions by thermodynamic principles. A further extension to the result was published by Hemar, Herrmann, Lemaréchal, Hocquart and Lequeux (1997). Later, McClements et al. (1999) and Chanamai et al. (1999) developed a core–shell model for the same system, including viscous effects and intrinsic absorption, and incorporated it into the existing ECAH/LB multiple scattering model. Hipp et al. (2002a, 2002b) also derived a core–shell model to account for both thermal and shear wave overlap effects within a multiple scattering model. These authors have demonstrated some success in matching theoretical predictions with experimental measurements for oil in water emulsions. However, the core–shell model does suffer from some disadvantages. The most general form provided by Hipp requires numerical solution of 12×12 matrix equation which is numerically badly conditioned; such complexity is inappropriate for use embedded in an in-line monitoring system. The analytical version derived by the McClements groups is not readily applied to polydisperse systems and was extended beyond the long wavelength region by using a conversion factor applied to the more general scattering coefficient solution.

In this paper we present an alternative approach to the thermal multiple scattering problem (thermal overlap), based on a generalized multiple scattering model of Luppé et al. (2012). Luppé et al. (2012) extended the multiple scattering model of Waterman and Truell (1961), which is similar to that of Lloyd and Berry (1967), by including the combined scattered thermal and viscous wave fields which had previously been neglected. As illustrated in Fig. 1, they considered the contribution of the scattered thermal and viscous waves to the wave field which is incident at a neighboring particle, and can be reconverted back into the compressional mode. Their mathematical result for the effective wavenumber has yet to be tested numerically and against experiment for typical colloidal and nanoparticle systems. The work reported here studies the contribution made by the additional thermal scattering terms which are significant for emulsions. The results of numerical calculations are compared with previously published experimental data.

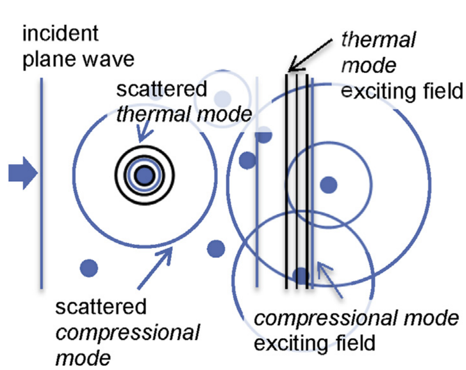

Fig. 1. Illustration of the superposition of scattered waves of compressional and thermal modes for an incident compressional plane wave. The scattered waves combine to form a plane wave of each mode after averaging over particle locations.

2. Methods

2.1. Ultrasonic scattering theory

The three wave modes which are considered in the ECAH/LB formulation are the compressional, thermal and shear modes, with wavenumbers

$$k_C = \frac{\omega}{v} + i\alpha \quad k_T = \left(\frac{\omega\rho C_p}{2\tau}\right)^{1/2}(1+i) \quad k_S = \left(\frac{\omega\rho}{2\eta}\right)^{1/2}(1+i) \tag{1}$$

where k is a wavenumber, with subscripts C, T, S denoting the compressional, thermal and shear mode respectively. The angular frequency is ω and the speed and attenuation of the compressional mode are represented by v and α respectively. Physical properties of the material are denoted by ρ for the density, C_p for the heat capacity, τ for the thermal conductivity, and η for the shear viscosity; $i = \sqrt{-1}$. It can be seen from the wavenumber equations, that the thermal and shear wave modes have equal real and imaginary parts, so that they lose $1/e$ of their amplitude in a distance of $\lambda/2\pi$ where λ is the wavelength.

The scattering of an incident planar compressional wave by a single spherical particle was expressed by Epstein and Carhart (1953) and Allegra and Hawley (1972) as a sum of partial waves (spherical harmonics multiplied by radial dependence functions). Their scattering coefficients, denoted by A_n, B_n, C_n for the scattered compressional, thermal and shear wave modes respectively, are the amplitudes of the scattered partial waves for each mode. Their notation can be generalized to an incident wave of any mode by use of a "transition operator", $T_n^{qp}(\mathbf{r})$, which defines the transformation of the incident plane wave into scattered waves of any mode. For an incident wave of mode q which can be defined by a scalar potential Φ (compressional and thermal modes), the planar incident field is expressed as

$$\Phi_{0q} = \sum_{n=0}^{\infty} i^n(2n+1)j_n(k_q r)P_n(\cos\theta)$$

and the scattered fields of mode p by

$$\Phi_{0p} = \sum_{n=0}^{\infty} T_n^{qp} h_n(k_p r)P_n(\cos\theta)$$

where p and q can be any mode C, T, S (shear wave modes require a vector potential, not a scalar potential as written here). The scattered fields are written using spherical coordinates $\mathbf{r} = (r, \theta, \phi)$ with origin at the particle center, j_n and h_n are spherical Bessel and Hankel functions respectively, and P_n denotes the Legendre polynomials. Thus the transition operator $T_n^{qp}(\mathbf{r})$ defines the transformation from incident to scattered fields thus

$$T_n^{qp}(\mathbf{r})j_n(k_q r)P_n(\cos\theta) = T_n^{qp}h_n(k_p r)P_n(\cos\theta)$$