14

Analysis of Droplet Characteristics Using Low-Intensity Ultrasound

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I. INTRODUCTION

A. Introduction

Sensory and bulk physicochemical properties of food emulsions, such as texture, stability, appearance, and taste are largely determined by the characteristics of the droplets that they contain (i.e., particle size distribution, disperse phase volume fraction, physical state, and colloidal interactions) (1). For example, the rate at which droplets cream or sediment due to gravitational forces is strongly dependent on their size. The characteristics of the droplets in a particular emulsion are governed principally by the ingredients it contains, the homogenization technique used to prepare it, and the environmental conditions it experiences during manufacture, storage, and consumption and may change appreciably during the lifetime of the product due to various instability mechanisms. For these reasons and because it is impossible to accurately predict the structure/functionality for many real systems, it is important to have analytical techniques that can be used to measure the characteristics of the droplets in emulsions.

The compositional and microstructural complexity of food emulsions often makes traditional methods of droplet characterization unreliable (e.g., microscopy, light scattering, and electrical pulse counting) Consequently, the development of novel methods of characterizing droplet characteristics in food emulsions has gained impetus in recent years. The ideal analytical technique for measuring droplet characteristics would be non-destructive, simple to use, versatile, rapid, reproducible, and reasonably priced. It would also be valuable to be able to make measurements on emulsions during the manufacturing process, so the technique should meet hygienic processing standards and be robust enough to survive in a factory environment. Analytical techniques based on ultrasound meet many of these requirements.

B. Ultrasonic Propagation in Food Emulsions

Analytical techniques based on ultrasound use high-frequency mechanical vibrations (typically between 20 kHz and 200 MHz) to provide information about the composition, structure, or dynamics of materials (2). Ultrasonic waves are qualitatively similar to sound waves, but their frequencies are too high for the human ear to detect. Ultrasonic waves propagate through materials as small deformations in the thermal–mechanical properties (i.e., as small deviations in the average temperature and pressure of the material). The power levels used in the ultrasonic analysis of food emulsions are so low that the deformations caused in the material are extremely small and reversible, which means that the technique is nondestructive.

In general, the most commonly used ultrasonic waves for characterizing materials are *longitudinal* waves and *shear* waves. In longitudinal waves, the deformations occur parallel to the direction of transmission of the wave, whereas in shear waves, the deformations occur perpendicular to the direction of transmission. The longitudinal ultrasonic properties of a material are fundamentally a function of the compressibility of a material and the amount of material to be compressed (i.e., density), Shear waves are highly attenuated in most fluids and so they are rarely used to characterize food emulsions and are not discussed further here.

The parameters that are most commonly measured in an ultrasonic experiment are the ultrasonic velocity, c, and the ultrasonic attenuation coefficient, α:

$$c = \frac{d}{t} = \lambda f \tag{1}$$

$$\frac{A}{A_0} = e^{-\alpha d} \tag{2}$$

where d is the distance traveled by the wave in t, λ is the wavelength of the ultrasonic wave, f is the frequency of the ultrasonic wave, and A and A_0 are the initial and final amplitudes of the ultrasonic wave. The overall ultrasonic characteristics of a material are represented by the complex propagation constant, $k = \omega/c + i\alpha$, where ω is the angular frequency ($=2\pi f$) and i is $\sqrt{-1}$. Velocity and attenuation are fundamental physical properties of the emulsion but are only useful if they can be measured accurately and related to the droplet properties of interest.

During recent years, there have been considerable advances in the development of mathematical theories to describe the propagation of ultrasonic waves through emulsions (3–5). These theories can be used to relate the measurable ultrasonic properties of an emulsion (i.e., c, α, or k) to the droplet characteristics of the emulsion (e.g., particle size distribution and dispersed phase volume fraction). A simplified version of the theory is presented here, which is suitable for application to relatively dilute emulsions containing nonflocculated droplets in the long-wavelength limit (i.e., $r \ll \lambda$) (5):

$$\left(\frac{K}{k_1}\right)^2 = \left(1 - \frac{3i\phi A_m}{(k_1 r)^3}\right)\left(1 - \frac{9i\phi A_d}{(k_1 r)^3}\right), \tag{3}$$

where K is the complex propagation constant of the emulsion ($=\omega/c + i\alpha$), k_1 is the complex propagation constant of the continuous phase, ϕ is the dispersed phase volume fraction, and A_m and A_d are the monopole and dipole scattering coefficients, respectively, individual droplets. Scattering coefficients appropriate for fluid-in-fluid colloidal dispersions and for solid-in-fluid colloidal dispersions are available in the literature (6). Nevertheless, calculation of these coefficients requires knowledge of many physiochemical properties of the oil and water phases (e.g., ultrasonic velocity, attenuation coefficient, specific heat capacity, thermal conductivity, density, and cubical expansion coefficient). The need for all of this information in order to interpret ultrasonic measurements is currently one of the major drawbacks of ultrasonic analysis techniques, although an increasing amount of data is being tabulated in the literature (7). The ultrasonic velocity and attenuation coefficient of an emulsion are determined from the complex propagation constant using the following relationships: $c = \omega/\mathrm{Re}(K)$ and $\alpha = \mathrm{Im}(K)$.

It is informative to examine the physical significance of the scattering coefficients (A_m and A_d) that appear in the theories used to model the ultrasonic properties of emulsions.

1. Monopole Scattering Coefficient, A_m

The droplets and surrounding liquid expand and contract to different extents in the presence of the pressure fluctuations associated with an ultrasonic wave (Fig. 1a). Consequently, the droplet pulsates relative to the surrounding liquid, thus generating a monopole pressure wave that propagates into the surrounding liquid. Most of this monopole wave is not detected in the forward direction, which leads to an increase in the attenuation of the emulsion referred to as the *monopole scattering loss*. In addition, because of pressure–temperature coupling, there is a fluctuating temperature gradient between the droplet and surrounding liquid that causes heat to flow backward and forward across the droplet interface. This process is usually irreversible because the heat flow into the droplet is less than the heat flow outward. As a result, some of the ultrasonic energy is converted to heat, which leads to an increase in the attenuation of the emulsion referred to as the *thermal absorption loss*. The distance that the thermal wave propagates into the surrounding liquid is characterized by the *thermal skin depth*, δ_T:

$$\delta_T = \sqrt{\frac{2\tau_1}{\rho_1 C_P \eta_1 \omega}} \tag{4}$$

where the angular frequency is ω, the density is ρ, the specific heat capacity is C_P, the thermal conductivity is τ, and the viscosity is η (subscript 1 refers to the continuous phase). This equation indicates that the thickness of the thermal wave increases as the frequency of the ultrasonic wave decreases.

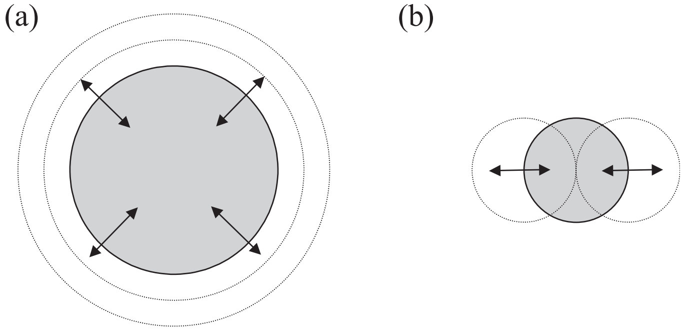

Figure 1 Diagram (not to scale) illustrating models of ultrasonic scattering from an emulsion droplet: (a) thermal (monopolar) scattering: (b) viscous (dipolar) scattering.

The thermal absorption loss is much greater than the monopole scattering loss in the long-wavelength limit.

2. Dipole Scattering Coefficient, A_d

As an ultrasonic wave passes through an emulsion, it causes the droplets to oscillate backward and forward because of the density difference between them and the surrounding liquid (Fig. 1b). The movement of the droplets relative to the surrounding liquid leads to the generation of a dipolar pressure wave. Most of this dipole wave is not detected in the forward direction, which leads to an increase in the attenuation of the emulsion referred to as the *dipole scattering loss*. In addition, the oscillation of the droplet is damped because of the viscosity of the surrounding liquid, and so some of the ultrasonic energy is lost as heat, which leads to an increase in the attenuation of the emulsion referred to as the *viscoinertial absorption loss*. The distance that the viscoinertial wave propagates into the surrounding liquid is characterized by by *viscoinertial skin depth*, δ_S:

$$\delta_S = \sqrt{\frac{2\eta_1}{\rho_t\omega}} \qquad (5)$$

This equation indicates that the thickness of the viscoinertial wave also increases as the frequency of the ultrasonic wave decreases (8). The viscoinertial absorption loss is much greater than the dipole scattering loss in the long-wavelength limit.

3. Limitations of the Theory

The above theory assumes that the emulsions are dilute enough so that multiple-scattering effects are unimportant and that the thermal and viscoinertial waves generated by one droplet do not overlap those generated by neighboring droplets (9). Multiple-scattering and viscoinertial overlap effects are usually quite small in food emulsions, but thermal overlap effects can be appreciable and lead to a significant reduction in the attenuation coefficient compared to that predicted by Eq. (3), (9). The deviations between theory and experiment increase as the ultrasonic frequency decreases, the particle size decreases, and the droplet concentration increases. For example, in Fig. 2, the simple theory set out in Eq. (3) predicts that attenuation should increase with droplet concentration, whereas the experimental observations indicate a maximum close to $\phi = 50\%$. Beyond this concentration, the thermal layers of adjacent droplets begin to overlap and each individual particle is less able to convert sound energy to heat;

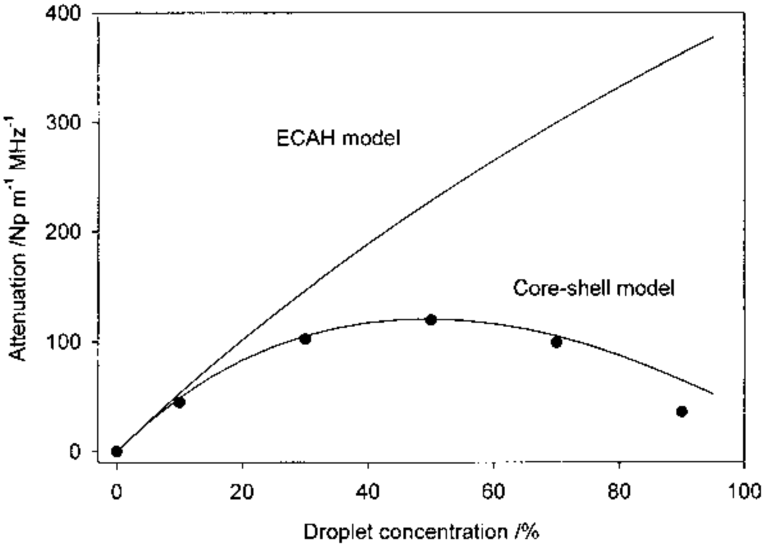

Figure 2 Ultrasonic attenuation coefficient (at 10 MHz) of an *n*-hexadecane oil-in-water emulsion ($r_{32} = 0.2\,\mu m$) as a function of emulsion concentration. Two theoretical lines are shown alongside the data: the Epstein–Carhart–Alegra–Hawley (ECAH) model and a more sophisticated core–shell scattering theory described in the text.

hence, the total attenuation is reduced. Similarly, when considering the attenuation spectra of different concentrations of fine (Fig. 3a) and coarse emulsions (Fig. 3b), the simple theory in Eq. (3) gives an adequate fit when the skin overlap is not significant (i.e., large, dilute particles at high frequency).

Recently, a number of methods of incorporating thermal overlap (10) and viscoinertial overlap (11) effects into the ultrasonic scattering theory have been proposed and combined to produce a comprehensive core–shell scattering theory that gives a good description of the ultrasonic properties of emulsions over a wide range of conditions (Fig. 2; the core–shell theory also gives a good description of the data in Fig. 3, but these lines are not shown here).

Another major limitation of the theory is that it assumes that the droplets are randomly dispersed in the emulsion. If the droplets undergo flocculation, then there may be an appreciable deviation between the ultrasonic scattering theory and experimental measurements because of thermal overlap and scattering effects. In a flocculated emulsion, the droplets are in close proximity, which leads to a greater degree of thermal overlap and a

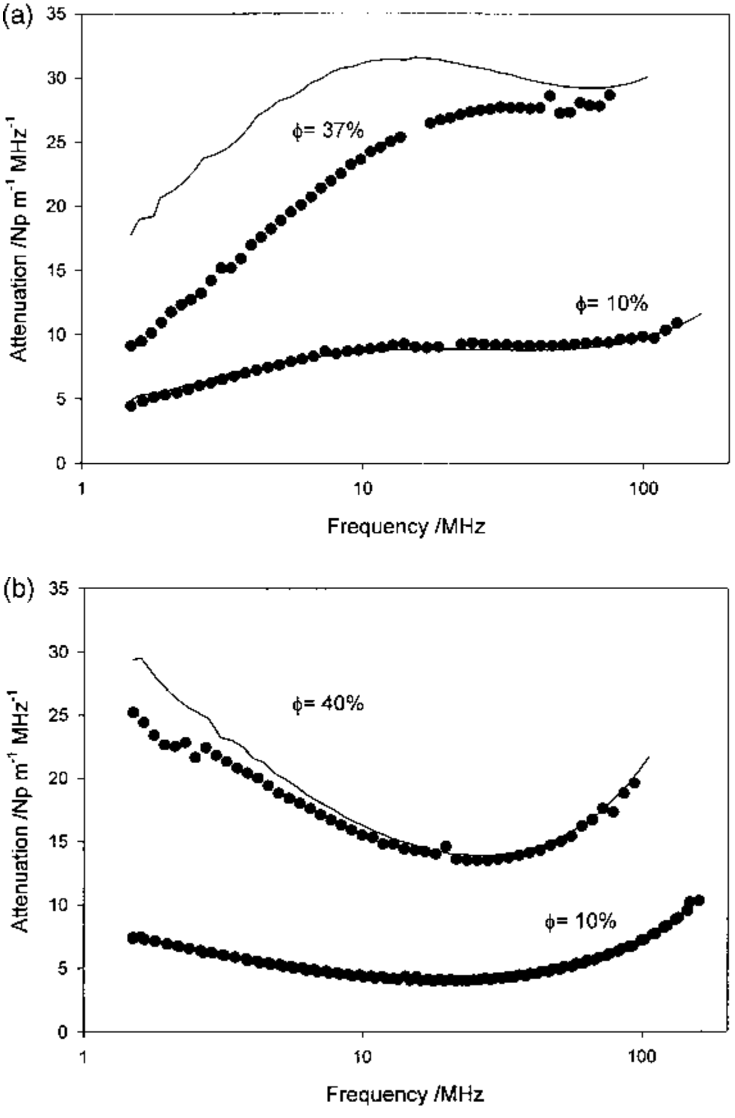

Figure 3 Ultrasonic attenuation spectra for different concentrations of silicone oil in water emulsions: (a) fine ($r = 0.1\,\mu m$) droplets and (b) coarse ($r = 0.56\,\mu m$). Theoretical prediction from ECAH multiple-scattering theory is shown alongside the experimental data.

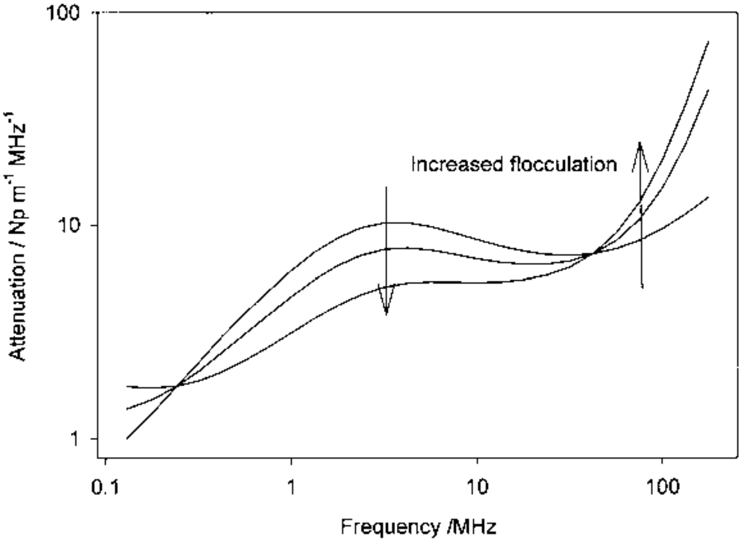

Figure 4 Theoretical prediction of the attenuation spectra of 10% silicone oil in water emulsions flocculated to different extents. The primary particle size is 0.25 μm and the floc size is taken as 5 μm, with a packing fraction of droplets inside the flocs of 63%.

decrease in the attenuation at low ultrasonic frequencies. In addition, the effective particles in a flocculated emulsions are larger than in a nonflocculated emulsion, which leads to increased scattering and attenuation at high frequencies (9) (Fig. 4). Recently, a theory has been developed to relate the ultrasonic properties of flocculated emulsions to floc characteristics, such as concentration, size, and internal packing (9). This theory assumes that a flocculated emulsion can be treated as a two-phase system, which consists of spherical "particles" (the flocs) dispersed in a continuous phase. The flocs are treated as an "effective medium" whose properties depend on the size, concentration, and packing of the droplets within them. The ultrasonic properties of a flocculated emulsion are calculated using a two-stage procedure. First, the thermophysical and ultrasonic properties of the effective medium within the flocs are calculated using a core–shell theory. Second, the ultrasonic properties of a suspension of these flocs dispersed in a continuous phase are calculated using ultrasonic scattering theory. Sample theoretical predictions of the attenuation spectra of flocculated emulsions are presented in Fig. 4. These were calculated assuming varying proportions of the droplets (diameter = 1 μm) were present in flocs (diameter = 10 μm). This theory has been shown to give good agreement with experimental measurements of flocculated oil-in-water emulsions (12).

Finally, it should be mentioned that the development, refinement, and validation of theories suitable for interpreting ultrasonic spectra of emulsions and other types of colloidal suspension is currently a highly active area of research (13–16). Therefore it is likely that further developments will occur in the near future.

C. Ultrasonic Measurements

Many of the ultrasonic methodologies developed for fluids characterization (17–21) are suitable for food emulsions. A typical experimental setup includes an electrical signal generator that is used to excite an ultrasonic transducer to produce an acoustic wave which, after passing through the emulsion, is detected by a second transducer. (Alternatively, a single transducer and a reflector plate may sometimes be used.) These components are arranged in two main groups: pulse and resonance methods.

1. Pulse methods. A pulse of ultrasound is measured after transmission through a known path length of emulsion. This ultrasonic velocity is determined by measuring the time taken for the pulse to travel a fixed distance [Eq. (1)], and the attenuation coefficient is determined by measuring the reduction in amplitude of the pulse after it has traveled through the emulsion [Eq. (2)] (17,22). The frequency dependence of the ultrasonic properties of an emulsion can be determined using two different pulsed techniques: tone burst and Fourier transform. In the tone-burst method, a pulse containing a number of cycles of ultrasound at a single frequency (actually a narrow range of frequencies) is applied to the sample, and the ultrasonic velocity and attenuation coefficient of the sample are determined at this specific frequency. This procedure is then repeated using ultrasonic waves with different frequencies. In the Fourier transform method, a broadband pulse of ultrasound, which contains a range of different frequency components, is applied to the sample. Fourier transformation is then used to determine the velocity and attenuation of the ultrasonic wave over the frequency range of the transducer. The major advantage of the Fourier transform method is that a spectrum can be obtained using a single ultrasonic pulse, which speeds up the analysis (22).
2. Resonance Methods. Analytical instruments based on the resonator method use a continuous ultrasonic wave, rather than an ultrasonic pulse, to determine the ultrasonic properties of a sample. One transducer measures signal intensity and the other generates a continuous wave of either constant wavelength while

> the path length is varied or variable frequency across a fixed path length. In a fixed-path-length resonator, a continuous wave containing a single, slowly increasing ultrasonic frequency is transmitted across the measurement cell. When the cell path length is an integer number of whole wavelengths, constructive interference occurs and there is a maximum in the detected energy (20,21,23). The shape and position of these resonance peaks can be used to calculate the ultrasonic velocity and attenuation coefficient of the liquid in the cell to very high precision.

Traditionally, analytical instruments for characterizing emulsion properties had to be constructed by researchers', however, a number of instrument manufacturers now supply analytical instruments based on ultrasound that are specifically designed for characterizing emulsion properties. There are a number of important practical considerations that should be taken into account when developing or selecting an analytical instrument for characterizing emulsion properties.

- The ultrasonic properties of most liquids are strongly temperature dependent and so it is important to use an instrument in which the temperature is precisely controlled (i.e., ±0.2°C or better).
- The measurement volume of commercial ultrasonic analytical instruments can vary from a few milliliters to several liters, which may be important if a sample is expensive or in limited supply.
- The measurement time may be important in systems where rapid kinetic measurements are required. Data acquisition is usually much faster for Fourier transform spectrometers than for 'tone-burst' or resonance spectrometers, enabling faster kinetic processes to be monitored.
- Many commercial spectrometers will automatically calculate particle size distribution and disperse the phase volume fraction of an emulsion from its measured ultrasonic spectrum. The theories used by commercial instruments to make this calculation vary widely and it is essential to ensure that the theory has been validated for the types of system under investigation.
- Whereas both velocity and attenuation can be readily measured, velocity tends to be more affected by imprecision in temperature and composition, so attenuation is often more useful for structural measurements.
- Probably the single most common reason for poor-quality ultrasonic measurements is the presence of small air bubbles trapped within liquids. The large impedance mismatch between air cells and the surrounding emulsion leads to extensive scattering of

ultrasound that can obscure the effects of the emulsion itself. In many cases, air cells can be eliminated by judicious use of gentle centrifugation or degassing prior to measurement.

II. APPLICATIONS

Studies over many years, usually using custom-built ultrasonic instrumentation, has demonstrated the potential of the ultrasonic technique for characterizing the properties of emulsion droplets (e.g., droplet size, droplet concentration, droplet crystallization, and creaming stability). Ultrasound has advantages over many alternative technologies because measurements are rapid, nondestructive, and noninvasive and can be made in concentrated or optically opaque materials. Recently, analytical instruments based on ultrasonic spectrometry that are specifically designed for characterizing emulsion properties have become commercially available. Consequently, many of the potential benefits of ultrasonic technology for characterizing food emulsions have become available to scientists working in the food industry. Nevertheless, it is important for users of these commercial instruments to be aware of the theoretical basis of the ultrasonic technique, because improper measurement procedures or data interpretation can lead to appreciable errors.

A. Droplet Concentration

Analysis of droplet concentration is one of the simplest and most successful applications of low-intensity ultrasonic techniques to food emulsions. This application is based on there being an appreciable difference in the ultrasonic velocities of the oil and aqueous phases when ultrasonic velocity measurements are used or there being a significant amount of attenuation of the ultrasonic wave due to the presence of the emulsion droplets when attenuation coefficient measurements are used. The influence of droplet concentration on the ultrasonic velocity and attenuation of a model food emulsion is shown in Fig. 2. The droplet concentration of an emulsion can be determined by developing an empirical calibration curve or by using an appropriate theoretical model. The ultrasonic scattering theory described earlier [ECAH theory, Eq. (3)] adequately predicts the effects of droplet concentration on the ultrasonic properties of emulsions, provided that thermal overlap effects are not appreciable (24,25) (i.e., $\phi < 10\%$ in this case), but when thermal overlap becomes important (small droplet sizes, low ultrasonic frequencies, or high droplet concentrations), a more sophisticated theory must be applied (24). Criteria for deciding whether these effect should be taken into account have been published in the literature (24). Ultrasonic measurements have previously been used to measure the droplet volume fraction of emulsified vegetable oil (26), milk (27), and salad dressings (28, 29).

B. Particle Size

Analytical instruments based on ultrasonic spectroscopy are gaining increasing acceptance for measuring the droplet size distribution of concentrated food emulsions. These instruments normally measure the ultrasonic attenuation coefficient (and sometimes the ultrasonic velocity) over a range of frequencies and then compute the particle size distribution (and volume fraction) that gives the best agreement between the measured spectra and that predicted by ultrasonic scattering theory. The suitability of a given instrument for a particular application largely depends on how accurately the scattering theory it uses to analyze the measured spectrum represents the ultrasonic properties of the emulsion being analyzed. In relatively dilute nonflocculated emulsions, there is excellent agreement between theory and experiment, and the measured particle size distributions are in close agreement with those measured by other technologies (24,25). However, when thermal overlap effects are important (e.g., in concentrated or flocculated emulsions), there may be appreciable differences between theory and experiment (Figs. 2 and 3), which would lead to large erros in any measured particle size distributions. For example, if the ECAH theory was used to characterize the concentrated emulsion in Fig. 3a, it would attempt to calculate the particle size (*r*) in Eq. (3) that would cause the theoretical line to best approach the measured data. However, under these conditions, the ECAH theory does not well describe the emulsion (particularly at low frequencies), so the particle size calculated would be meaningless. Therefore, one should always ensure that the ultrasonic scattering theory being used to interpret the data is appropriate for all sizes, concentrations, and frequencies (24).

One should also be aware that in order to compute the droplet characteristics from the measured ultrasonic spectrum in a reasonable time, it is often necessary to make some simplifying assumption about the shape of the particle size distribution (e.g., it is monomodal or bimodal or has a log-normal form). Only if these assumptions about the shape of the particle size distribution are incorrect will the final data be inaccurate. Despite these limitations, ultrasonic spectroscopy is currently one of the few practical methods of measuring the droplet size distribution of concentrated emulsions in situ [other techniques include nuclear magnetic resonance (NMR), electroacoustics, diffuse optical reflectance, and dielectric spectroscopy] (1). The ultrasonic technique has been used to determine particle size distributions in a number of food products, including emulsified vegetable oils (30), salad cream (29), and milk fat globules (27).

C. Droplet Flocculation

The bulk physicochemical properties of many food emulsions are strongly influenced by droplet flocculation (e.g., creaming and rhelogy) (1) . It is therefore important to have analytical techniques capable of providing information about the extent of droplet flocculation and about the structural characteristics of the flocs formed. Characterization of floc properties in most food emulsions is extremely difficult because their delicate structure is disrupted by the sample preparation procedures required by many analytical techniques (e.g., dilution or stirring in light scattering, electrical pulse counting, or microscopy techniques). A number of studies have shown that the ultrasonic properties of emulsions change appreciably when the droplets become flocculated (8,31–33) and ultrasonic attenuation spectroscopy has been used to study droplet flocculation in oil-in-water emulsions induced by diverse mechanisms (12,34,35) in the light of recent theoretical developments (9).

The same ultrasonic spectroscopy technique has been used to study the disruption of flocs in a shear field (36). As the emulsions are exposed to higher shear rates, the flocs become disrupted and their attenuation spectra becomes closer to that of nonflocculated droplets. The sensitivity of ultrasonic spectra to droplet flocculation and the fact that ultrasonic techniques can be applied nondestructively and noninvasively opens up the potential for “rheo-acoustic” techniques (37,38). These techniques measure the rheology of colloidal dispersions using a conventional rheometer while obtaining information about the structure and concentration of flocs using an ultrasonic spectrometer. Thus, it is possible to correlate changes in dispersion rheology to changes in floc structure as the shear rate applied to the system is varied in a controlled manner.

D. Gravitational Separation

Creaming leads to a change in oil distribution throughout a product. Ultrasonic velocity (or attenuation) can be used to measure the concentration of oil in an emulsion (see Sect. II.A) as a function of height using a simple one-dimensional imaging apparatus. A stepper motor moves an ultrasonic transducer along the vertical axis of the emulsion and a series of ultrasonic measurements are made at different heights and times (39). The ultrasonic measurements can then be converted into oil concentrations using a calibration curve or ultrasonic scattering theory. A typical creaming profile

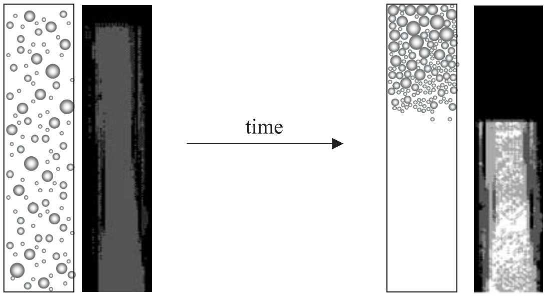

Figure 5 Diagrams and ultrasonic images illustrating creaming in oil-in-water emulsions. In the ultrasonic images, light regions indicate low oil content and dark regions indicate high oil content. Initially, the droplets are evenly dispersed and the ultrasonic image shows no detail. After storage, the droplets accumulate at the top of the container and a clear light/dark band is seen in the ultrasonic image.

for emulsified corn oil is shown in Fig. 5. In this case, the ultrasonic data are given as a two-dimensional image taken across a sample of emulsion at different times after preparation. Light areas indicate a higher oil concentration. This type of approach often has limited spatial resolution because the sound beam has a significant width (often ~1 cm) and averages the ultrasonic properties over that distance. It would be possible to achieve better resolution with a focused transducer or more sophisticated signal processing. It is important to remember that converting an ultrasonic measurement to oil concentration is not straightforward, as both particle size and oil concentration can vary within a cream layer and both can affect the ultrasonic signal (40–43). Even with these limitations, the use of ultrasonics to probe the structure of cream layers is a powerful tool and one of the unique applications of the technique. Conventional measurements of creaming are often based on visual identification of the boundary between and oil-rich layer and oil-poor layer and can easily miss details of fine structure. For example, xanthan gum can cause an emulsion to cream due to depletion flocculation (8), but there are a variety of structures formed within the cream layer not evident to the naked eye. Ultrasonic imaging of the process was also able to detect the influence of added salt on the structure of the cream layer induced in the emulsion by xanthan gum (44).

E. Droplet Crystallization

Ultrasound has proved to be a highly sensitive method for monitoring the melting and crystallization for emulsion droplets (45,46). The physicochemical basis of the utilization of ultrasound for this purpose is the relatively large difference in physical and ultrasonic properties of solid and liquid droplets.

The influence of heating and cooling on the ultrasonic velocity and attenuation coefficient of an *n*-hexadecane oil-in-water emulsion is shown in Fig. 6. When an emulsion containing crystalline fat droplets is heated, there is a sharp decrease in the ultrasonic velocity around the melting point of the bulk fat because the solid phase has a higher ultrasonic velocity than the liquid phase. When the same emulsion containing liquid oil droplets is cooled, the droplets exhibit a high degree of supercooling before they crystallize and the ultrasonic velocity returns to the starting solid-fat line. The emulsion droplets do not crystallize until they are cooled well below their thermodynamic melting point because the impurities that normally promote heterogeneous nucleation in bulk oils are distributed throughout such a very large number of droplets that each individual droplet is free of impurities. Consequently, nucleation tends to take place by a homogeneous mechanism (or sometimes a surface heterogeneous mechanism) in emulsions rather than be promoted by impurities as in bulk oils (47). To a first approximation, the fraction of crystalline material within the droplets (Φ) at a particular temperature can then be calculated as

$$\Phi = \left(\frac{1}{c^2} - \frac{1}{c_l^2}\right) \bigg/ \left(\frac{1}{c_s^2} - \frac{1}{c_l^2}\right) \qquad (6)$$

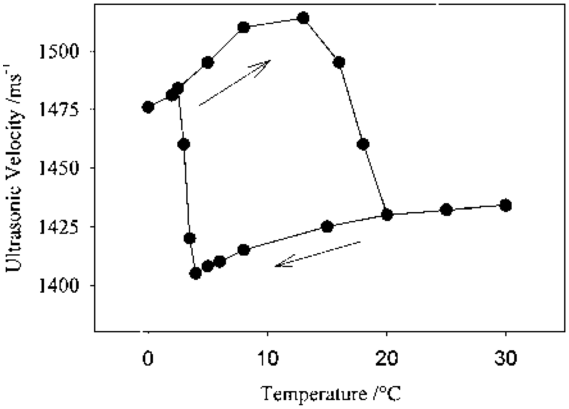

Figure 6 The effect of a cooling–heating cycle on the ultrasonic velocity in a 20% hexadecane-in-water emulsion. The speed of sound in the emulsion decreases with temperature and there is an abrupt change corresponding to the phase transition in the droplet oil. Supercooling of the liquid oil is responsible for the hysteresis loop observed.

where c is the measured ultrasonic velocity of the emulsion and c_s and c_l are the ultrasonic velocities in the emulsion when the droplets are completely solidified or completely liquefied oil, respectively, extrapolated to the measurement temperature (48). Equation (6) is based on the assumption that solid fats and liquid oils have similar densities and behave ideally as a mixture (49). Ultrasonic methods have been successfully used to measure the supercooling of emulsified triacyl glycerols (45,48), margarine and butter (50), and milk fat (49).

A similar hysteresis loop occurs in the attenuation coefficient of an emulsion during the melting and freezing of the droplets (51). However, in the experiment reported in Fig. 6 there was a large attenuation peak and extensive velocity dispersion at the melting point of the dispersed phase. This occurs because pressure–temperature fluctuations associated with the acoustic wave perturb the solid–liquid equilibrium and some of the ultrasonic energy is lost as heat. The magnitude of the attenuation peak is dependent on the frequency of the ultrasound. At low frequencies, the temperature–pressure gradients associated with the ultrasonic wave are small and so the equilibrium is maintained and attenuation is low. At high frequencies, the changes in temperature and pressure occur so rapidly that there is no time for the system to respond and the ultrasonic absorption is also low. However, at intermediate frequencies, the temperature–pressure gradients are sufficiently large and persist for a sufficiently long time that an appreciable amount of material is able to undergo an ultrasonically induced phase transition. The energy required to rapidly crystallize and melt a proportion of the fat leads to the significant absorption of the ultrasonic wave observed. The excess absorption is related to the dynamics of the phase transition (52).

III. CONCLUSIONS

The ultrasonic properties of emulsions are relatively easy to measure to good precision, particularly considering the wide commercialisation of acoustic spectrometers suitable for fluids characterization. The development of off-the-shelf instrumentation has been accompanied by advances in the theory describing ultrasonic spectra of emulsions in terms of particle size, concentration, association, and distribution. By comparing theory and experiment, it is possible to measure dispersed phase volume fraction, particle size (and, to some extent, particle size distribution), degree of flocculation, and creaming. Although examples of these measurements have been reported in the literature, rarely have multiple unknowns been deconvoluted from a single acoustic spectrum and so comprehensive ultrasonic characterization of droplet properties remains elusive. It is probably more practical to use ultrasound in conjunction with other established methods that can measure other properties (e.g., density measurements to calculate dispersed phase volume fraction and light scattering to calculate primary particle size) and then use the acoustic data to measure emulsion properties not otherwise readily accessible (e.g., flocculation).

Very often our understanding of the world jumps forward when we develop a new way of looking at it. As an example, consider the widespread introduction of static light-scattering instruments into food emulsions laboratories over the past 20 years. The theories and phenomena important in food emulsion science did not change, but the explanations used began to more specifically describe events in terms of the size of the structures present. In this example, the principles of light scattering had a long history, but the difficulty of making measurements and the complexity of the mathematics prevented widespread application until they were integrated into a convenient package.

Ultrasonic instruments for particle characterization are in a similar position now as light-scattering instruments were 20 years ago and we can expect a similar pattern of development. Using these methods, we can reasonably measure realistic concentrations of fat in a relatively undisturbed state and, hence, evaluate the real properties of delicate structures that our existing techniques necessarily disrupt in sample preparation. It is our hope that this chapter will go some way to encouraging food emulsion scientists to gain the benefits of the new approaches while avoiding some of the pitfalls of poor measurement technique or extension of a theory beyond its assumptions.

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