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Applications of ultrasonics in food science - novel control of fat crystallization and structuring

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Abstract

Low power (< 10 W m^{-2}) ultrasound spectroscopy has been used for many years for the characterisation of food colloids with respect to particle size distribution, adiabatic compressibility, particle solvation and dissolution, crystal nucleation and solid content. Whilst high power (>1 kW m^{-2}) ultrasound methods are well-known to impact on fat crystallization and structuring, they have many drawbacks, causing off-flavours through product oxidation and a metallic taste probably associated with sonotrode wear. Furthermore, process development with power ultrasound is hit and miss, applications being largely empirical and poorly understood. We have recently shown that well-controlled and understood crystal nucleation control can be obtained using well-defined low power, quasi-continuous ultrasound and acoustical pressure fields, opening up a new field of application in food processing for ultrasonics.

1 Introduction

The use of low power ultrasonics in food science extends over nearly forty years and in this author's case can be traced back to 1981[1]. Acoustical analysis of food structure including objective measures of human sensory perception is now a lively topic[2][3][4][5]. High power applications can be traced back to 1959[6].

The application of ultrasound techniques to fat crystallization and structuring can be traced back to work by Miles and Fursey in Bristol[7] which was then further developed in Leeds in conjunction with Eric Dickinson and Julian McClements[8]. A recent view of where Eric Dickinson pointed me to through his development of the subject of food colloids can be found in[9]. Work in the area has continued continuously since then and developments are summarised in two recent papers[9][10].

This review is mostly confined to developments in the past five years.

Ultrasound in food science may conveniently be divided into two areas[11]: low power (< 10 W m^{-2}) for material characterisation and high power (>1 kW m^{-2} and > 10 kW m^{-2} for cavitation in aqueous systems) for material modification and processing. However, it has recently been shown that under some special circumstances, even low power ultrasound may be material altering[10].

A recent review of ultrasound in food technology[12] gives a comprehensive, albeit uncritical, overview covering applications in filtration, freezing and crystallization, de-frosting and thawing, de-foaming, degassing, de-aeration, cutting, drying, tempering, bleaching, cooking and sterilization, extraction, mixing, de-polymerization, de-moulding, extrusion, meat tenderization, brining, pickling, marinating, emulsification, homogenization and enzyme inactivation. A better although less cited review is that by Awad et al[13] which also addresses low power ultrasound applications and theory. The processing effects described in these reviews are achieved mostly in an empirical manner through a range of sometimes contradictory processes associated with power ultrasound creating stable and transient cavitation[14]; free radical production and intense shear are also associated with bubble collapse in transient cavitation.

Below we consider the relationship between fat crystallization and fat structure and consider the role of both high power and low power ultrasound in the control of fat crystallization and structure.

2 The Relationship between Fat Crystallization and Fat Structure

The macroscopic structure of foods containing fats such as margarine, fatty spreads, butter, mayonnaise and ice cream may be viewed as the emergence of different structures at different scales. At the smallest scale, that of individual molecule surrounded by similar molecules, all objects are in motion and without a fixed position relative to each other. Even here things are not so simple, for example if we take the case of water each water molecule as it tumbles around sees on average a structured environment with a higher density of molecules co-ordinating with each of the hydrogens. here, the crystalline unit cell, the individual crystal habit and the morphology associated with many separate crystals forming a space filling network which imparts rigidity and structure on the product. During the manufacture of a fatty spread an oil-in-water emulsion is first produced in which crystal nucleation is initiated. The transformation from the disordered liquid state to an embryonic then stable solid nucleus was recently discussed in [10] and what appears there will not be repeated here.

Distinguishing the point at which a solid state has emerged in an oil or any saturated solution (The solid state of a pure material may be regarded as emerging from a saturated solution of itself) has created a great deal of discussion and here ultrasound has a lot to offer. The speed of sound in any material can be described by the relationship:

$$c = \sqrt{Elastic\ constant\ M / Density\ \rho}$$

In solid material the elastic constant comprises a bulk modulus K and a rigidity modulus G.

$$c = \sqrt{(K + {}^{4}/_{3}\, G) / \rho}$$

In a fluid such as water $K \approx 10^{10}$ Pa whilst even in food gels $G \approx 1 - 10$ Pa. So the speed of sound in fluids is well described by the Wood Equation

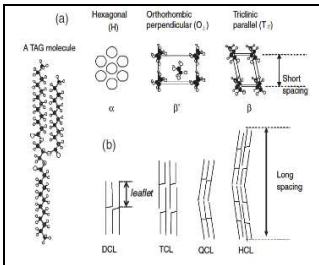
$$c = \sqrt{K/\rho} = \sqrt{1/\kappa\rho}$$

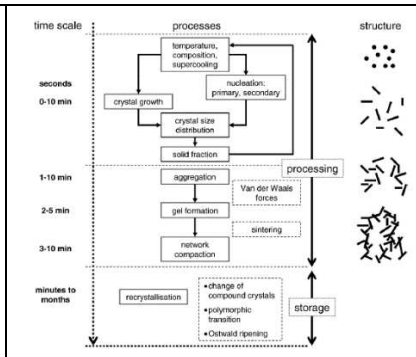
Where κ is the adiabatic compressibility.

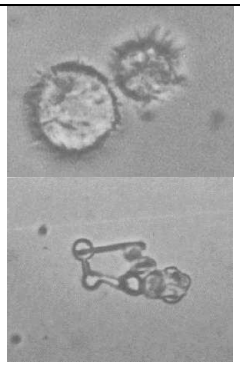
It is not only the density that undergoes a first order transition through the liquid-solid phase transition but also the adiabatic compressibility (G increases from a few Pa to the same order as K). Since the speed of sound can be measured routinely in a manufacturing process to 5 significant figures (in-line density measurements are not so easy to make and the changes in density are smaller) very accurate determinations of the initial appearance of solid nuclei from a cocoa butter melt can be made (See also Figure 4 below). Some time ago we measured the effect of cocoa butter seed crystals on cocoa butter crystallization and the impact of these seed crystals on the chocolate tempering process is still widely ignored throughout the chocolate confectionery industry despite its impact being well-known, albeit poorly understood [15][16,17]. Yet, removal of the seed crystals from the melt suppresses nucleation of the required Form V.

Thus far our discussion has confined itself to the first stage (1) in Figure 1.

As shown in Stage (2) of Figure 1 initially the crystals grow individually out of the oil droplets they begin to stick to each other (Figure 1 – (3)) and the emulsion inverts as the solid structure fills space and the water becomes dispersed as small droplets within a continuous fat matrix (Figure 1 – (4)), locking them away from microbial and mould growth and imparting on the resulting material a soft solid structure with desirable organoleptic properties.

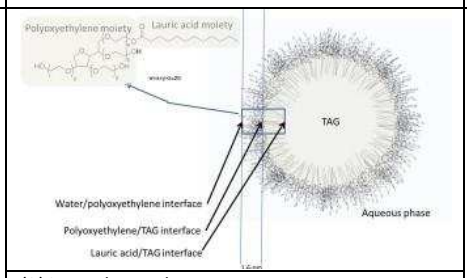






(1)Molecular structure and molecular packing

(K. Sato, S. Ueno / Current Opinion in Colloid & Interface Science 16 (2011) 384–390)



(2)Crystal growth
(top: Himawan C, Starov VM, Stapley a GF. Thermodynamic and kinetic aspects of fat crystallization. Adv Colloid Interface Sci 2006;122:3–33. doi:10.1016/j.cis.2006.06.016. Bottom [1] Povey MJW. Crystal nucleation in food colloids. Food Hydrocoll 2014;42:118–29. doi:10.1016/j.foodhyd.2014.01.016.)

(3)Emergence of space filling structure mediated through crystal-crystal-oil-water surface energy, interaction and morphology
(P. Walstra and K. Boode, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 81 (1993) 121-137)

(4) Development of complete soft solid structure on completion of crystal growth -Margarine

Scale increasing from (1) ~ nm through (2) micrometers and (3) millimetres to (4) centimetres

Figure 1Emergence of structure as scale increases from the molecule through a single crystal and interacting crystals to a solid structure containing liquid

In chocolate, the creation of the correct polymorph is essential to the production of a stable product with a long shelf life and attributes such as glossiness, mould release, snap, cooling in the mouth and a sharp melting point. Ultrasound offers many opportunities to study these processes at the various scales at which they occur and current methods for doing this are reviewed in Section 4.

Recently a lot of attention is being given to the stereochemistry of fats and its implications for structuring[18,19].

3 High power ultrasound control of fat crystallization and structuring

A useful diagram is provided below in Figure 2 from Johannsson et al[20] gives some idea of the power levels involved in applications of power ultrasound.

Fundamental studies of power ultrasound are few and far between (but see [21] and [20]) which is a disadvantage because high power ultrasound induced cavitation is a complex process (See Section 3.1 below), difficult to characterise and control. Transient cavitation fields behave chaotically and generate high levels of free radicals in aqueous systems, leading to often undesired oxidative effects[20] which have led to the abandonment of many otherwise promising food industrial applications. The chaotic behaviour of cavitation fields arises from a huge acoustic mismatch between the bubbles produced and the acoustic field, leading to growth and collapse of the cavitating field in difficult to predict ways. Where sonotrodes are used, wear of the sonotrode introduces contamination of the food with the sonotrode material.

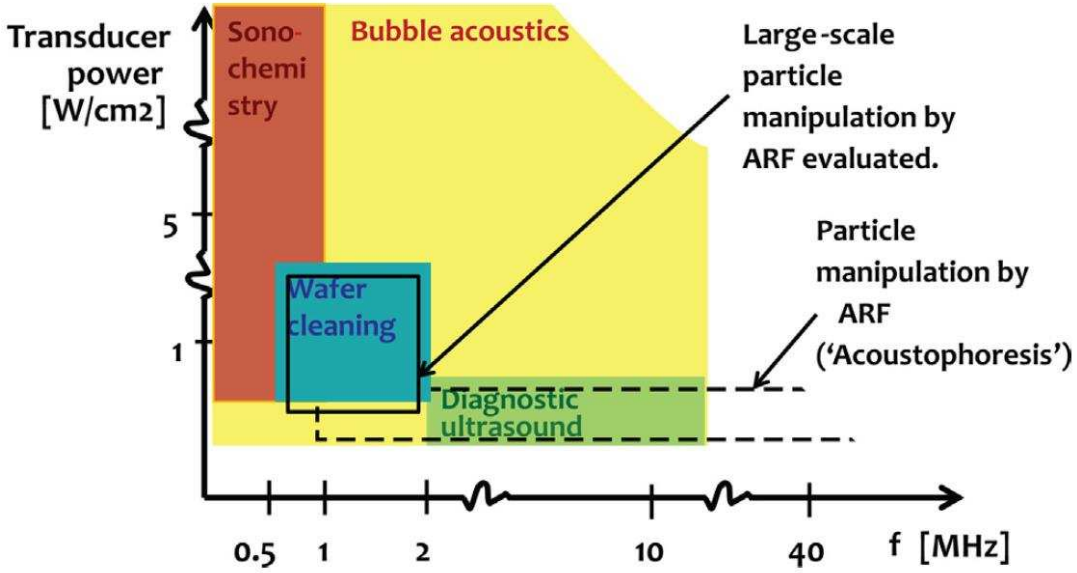


Figure 2 Empirical delineation of power-frequency combinations deployed in various applications of ultrasound (reproduced with permission from Ultrasonics Sonochemistry, Volume 28, January 2016, Pages 346–356.

A contradiction arises because on the one hand the high shear and the production of free radicals promotes desired processes such as sterilization, on the other hand in sono-crystallization of fats, free radical production leads to highly undesirable oxidation and oxidative rancidity. In addition, acoustic radiation forces operating independently of cavitation and also at lower powers create streaming and particle fractionation effects.

3.1 Sono-Crystallization

The well-known impact of sono-crystallization is also contradictory, small changes in power can result in a change from the nucleation of crystals to their melting. We have shown that even a stably oscillating bubble can nucleate crystallization[22–24], if the insonifying power is slightly increased, the crystals so created can then be melted!

Despite recent research into power ultrasound applications in food being very active with over 25 papers per year being published over the past five years, the disadvantages of high power ultrasound are rarely referred to although anecdotal evidence provided to the author by industrial scientists from a number of companies suggest the abandonment of a number of large projects for the reasons given above; the use of power ultrasound in the processing of chocolate and cocoa butter being a case in point. Power ultrasound is not used to anything like the extent expected from recent reviews[3]; in a recent comprehensive review of the production and refining of oils and fats; only one reference could be found to the use of ultrasound and that was to do with the de-gumming of oil[25].

4 Low power control of fat crystallization and structuring

4.1 Ultrasound velocimetry

Low power ultrasound involves the use of pulsed or quasi-continuous ultrasound pressure waves between about 20 KHz and 200 MHz at power levels below 10 W m^{-2}. This level is well below the level used even for diagnostic ultrasound shown in Figure 2 and is off the scale in that Figure. To put this in perspective, The first commercial instrument designed for the monitoring and control of fat crystallization was built in conjunction with Unilever and was called the Cygnus Ultrasound Velocity Meter or UVM. This device uses a technique called pulse echo whereby a single transducer both generates the ultrasound pulse and detects it. The pulse travels a known distance and its time of flight is measured digitally, so that the speed of sound is calculated automatically by dividing distance by time. The distance is accurately determined by filling the cell with de-ionised

water in which the speed of sound is well known. Accurate measurement of temperature is important because the temperature coefficient of the speed of sound in water is 3 m s^{-1} K^{-1}. Ultrasound velocimetry can be expected to give an accuracy of better than 1 m s^{-1} and a precision 10X better than that, so it is the temperature control which is the most important determinant of accuracy and the four wire RTD provides an accuracy of around 0.2 K.

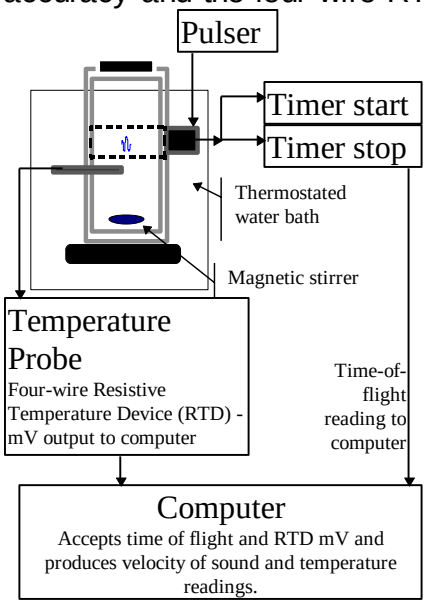


Figure 3 Diagram of the Cygnus UVM ultrasound velocity meter

Very high precision, repeatable measurements of crystallizing emulsions can be used with this system and an example is given in Figure 4 to Figure 6.

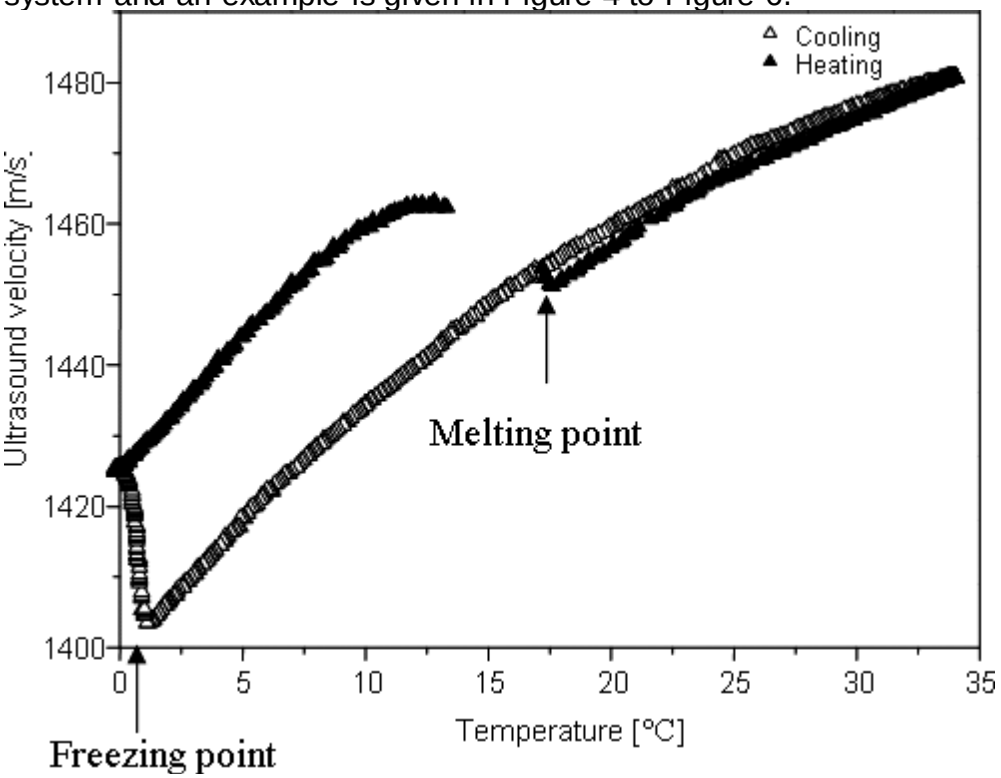


Figure 4 Temperature dependence of the ultrasonic velocity of a 5-wt-% n-hexadecane-in-water emulsion stabilised by 0.5 wt-% Caflon phc060 during cooling and heating at a constant rate of 1 K/min.[26]

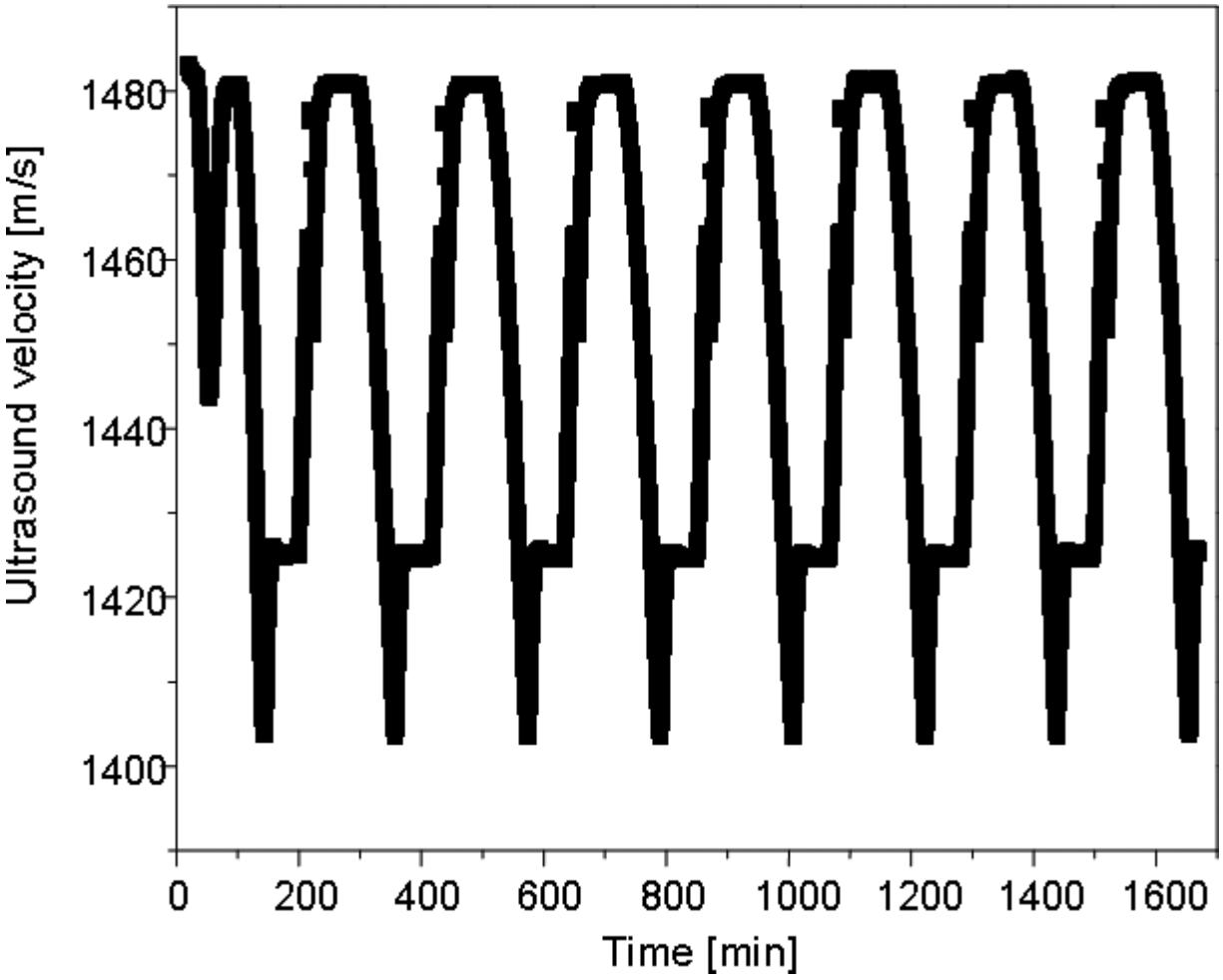


Figure 5 Illustration of emulsion stability through repeated crystallisation and melting of the emulsion in Figure 4. The velocity of sound is plotted against time whilst the emulsion is repeatedly cooled from 35 to 0 ^{o}C and then heated back to 35 ^{o}C.[26]

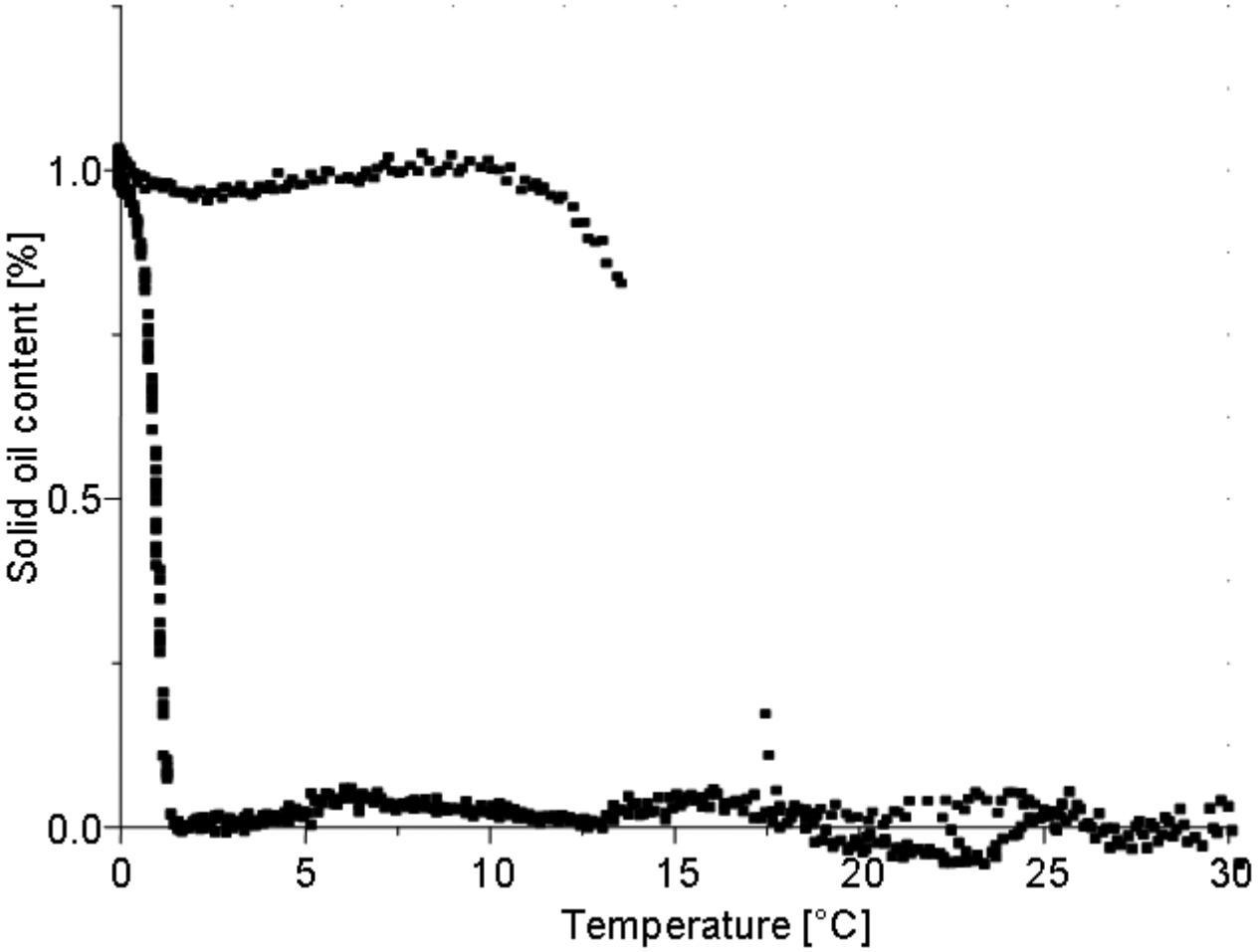


Figure 6 Temperature dependence of the solid content determined from the ultrasound velocity data in Figure 4 [26]

This device and ones similar to it are extensively used in our laboratory to study nucleation kinetics, solid fat content in emulsions and crystallizing fats and this work is extensively reviewed in [9]. It is important to be aware that once crystals sinter and networks appear the acoustical theory is not so well defined since an additional parameter called the frame modulus appears[27], nevertheless, the point at which the system begins to gel can easily be identified through departures from the normal acoustical behaviour of independent, non-interacting, crystals.

Ultrasound velocimetry is a also powerful method for following powder dissolution and the subsequent solvation of powder[28][29] and we have recently used this to study the dissolution of powders containing fluorescent compounds which cannot be followed using Ultra-Violet turbidity measurements.

4.2 Ultrasound attenuation spectroscopy

A comprehensive description of ultrasound attenuation spectroscopy can be found in [30]. In the case of the Malvern Ultrasizer which we use extensively to measure particle size in concentrated oil-in-water and fat-in-water emulsions the frequency extends between 2 MHz and 120 MHz and the ultrasound attenuation is measured as a function of frequency to give the attenuation spectrum. The spectrum can then be inverted, with sufficient knowledge of the physical properties of the material, to give a particle size distribution without dilution and under stirred conditions, which reports particle sizes between 10 nm and 1 mm. For example, we have sized whole milk, separately sizing the protein particle size distribution and that of the milk fat globules[31][32]. Attempts to use this technique to size crystals during growth have not been overly successful despite considerable effort [33–41]because the phase transition itself introduces an additional attenuation term, over and above the scattering terms[30] [42](thermal and visco-inertial) currently included in the inversion models. As a result, empirical methods of analysis were resorted to which suffered from the complicated and variable interaction between the ultrasound field and the

crystallising material, we now know that the quasi-continuous acoustic fields can modify the crystal nucleation process[43] and Section 4.3.1 below,

An advantage that ultrasound attenuation spectroscopy enjoys over light scattering techniques is its ability to measure concentrated systems and in stirred conditions, so that the emergence of structure can be followed over time. We are currently using this technique extensively to follow aggregation processes in milk.

4.3 Ultrasound control of fat crystallization

The problem with most studies of the impact of power ultrasound in food processing is that the physics (as opposed to the food science) is largely ignored, the most expected from a characterisation of the acoustic field being its frequency and the electrical power setting and sometimes even these elementary parameters are omitted. A few studies measure the heat flow by calorimetry and there have been attempts to map the field distribution. Others have used indicators such as alpha-amylase to chemically map the distribution of the cavitation impact[44] [21] . It is the chaotic nature of the transient cavitation which is the biggest obstacle to accurate field definition which is a pre-requisite for any good engineering design of a process. Acoustically the situation is greatly complicated by the fact that the insonifying acoustic frequencies are transformed into harmonics, subharmonics and partial harmonics through the complicated motion of the bubble surface, resulting in an entire spectrum of frequencies despite the input of a single frequency.
Ultrasound may have an impact at all the scales in Figure 1.

4.3.1 Scale (1) Figure 1 Low Power Quasi-Static Ultrasound

The phrase ‘low power quasi-static’ means power levels well below the cavitation threshold whose frequency remains constant over many cycles of the insonifying field as opposed to frequency varying or pulsed systems where only a very few cycles of sound are deployed at any one frequency. We have recently shown that these quasi-static fields have the potential to control nucleation and offer great promise because the method is underpinned by a mathematical model well founded in physics, although what has been published so far is far from the last word on the subject[43].

At the molecular scale, ultrasound (both high and low power) may influence nucleation [10], at low power the effects are predictable due to the rectification of heat transfer from a quasi-static pressure field changing the energy barrier to nucleation. The effect of high power, whilst undeniable, is far less predictable and in practice can only be developed empirically, this being the case over all length scales.

Low power pulsed ultrasound velocimetry (Section 4.1) has the potential to monitor the nucleation process simultaneously with the application of a low-power quasi-static ultrasound field, providing precision control over the nucleation process with the potential to transform fat crystallisation processes.

4.3.2 Scales (2) to (3) Figure 1

In the early stages of crystal growth, post nucleation, low power quasi-static ultrasound is unlikely to have any effects. Once crystal growth ensues the heat evolved raises the temperature, reducing undercooling and removing the energy barrier to crystal growth which pumping from the quasi-static acoustic field reduces or increases[10].

High power ultrasound has the potential to disrupt the sintering of crystals and secondary nucleation[9], breaking up crystal networks and altering the morphology and final structure of the product (Scale 4). However, the disadvantages of high power ultrasound have prevented this approach in fatty systems. It is possible that sub-cavitational fields can be used to achieve such desired modification of the networks with power levels at the lower end of Figure 2.

Again such material altering ultrasound processes may be combined with low power ultrasound monitoring techniques (Section 4.1) to give precise control over the later stages of the evolution of structure in fat containing systems.

5 Conclusion

Here we have discussed the application of ultrasonics in food science with a particular emphasis on the control of fat crystallization and structuring. It is shown that, despite considerable effort (25 publications per year for the past five years) power ultrasound has had little impact on the control of fat crystallization and structuring. The reasons for this are (a) the complex and poorly understood detailed physics involved; (b) generation of free radicals promoting oxidation of fats; (c) high shear associated with bubble collapse in transient cavitation which gives rise to wear of sonotrode and processing equipment, causing contamination of product and (d) the complex interaction between an oscillating bubble surface in stable cavitation, crystal nucleation and crystal growth. For this reason, it is suggested that future developments will take place at power ranges well-below those likely to produce cavitation or probe wear.

Low power ultrasound material characterisation techniques (Sections 4.1and 4.2) avoiding quasi-static excitation have the potential to transform the processing of fats, providing information on the early stages of crystal nucleation and growth, although providing only qualitative information in the later stages of the development of structure[27]. A recent development in ultrasound technology deploying Golay coded sequences to encode the generated acoustic signal offer promise for the future because the coding involves a continually altering frequency which allows much lower output powers due to improved signal to noise[45].

Whilst ultrasonic attenuation spectroscopy has great potential for sizing and particle characterisation concentrated systems such as oil-in-water and water-in-oil emulsions and can certainly be used where crystal growth is confined to the dispersed phase, the emergence of a frame modulus once crystal networks form are likely to restrict the technique to measurement up to including the emergence of a shear modulus associated with gelation or a crystal network.

Low power quasi-static ultrasound devices are likely to have a big impact in future due to the possibilities they offer for nucleation control. The future for high power ultrasound in fat crystallization and structure is likely to be confined to the early stages in the processing of fats and oils such as the de-gumming process, where later refining steps can ameliorate the negative effects of cavitation and equipment erosion. However, intermediate power, sub-cavitational ultrasound may permit the modification of morphology and structure in the later stages of crystallisation.

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Support for parts of this work from the EPSRC in the form of grant EP/M026310/1 is acknowledged; discussions with my colleagues on that project “Ultrasonic propagation in complex media: correlated spatial distributions and multiple dispersed phases” have influenced my thinking in this review (Dr Valerie Pinfield, Dr Will Parnell – Loughborough; Professor David Abrahams and Dr Artur Gower – Manchester as well as my colleagues in the School of Food Science and Nutrition here at Leeds, especially Dr Rammile Ettelaie and Dr Mel Holmes). Finally, a collaboration financed at Leeds by Lewtas Science and Technology has been particularly influential in the development of the low power quasi-static technique.

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