

ULTRASOUND FOR CHARACTERIZING COLLOIDS

Particle Sizing, Zeta Potential, Rheology

Andrei S. Dukhin and Philip J. Goetz

We would like to announce the publication of a new book, entitled

“ULTRASOUND for CHARACTERIZING COLLOIDS - Particle sizing, Zeta Potential, Rheology”

- 425 pages, 475 references, by A. Dukhin and P. Goetz. This book is being published as the next volume in the Elsevier series “Studies in Interface Science”, edited by D. Moebius and R. Miller. It has been submitted to Elsevier and should be published by July 2002.

You will find the Table of Contents and Introduction below.

Table of Contents

CHAPTER 1. Introduction	1
1.1 Historical overview.	5
1.2 Advantages of ultrasound over traditional characterization techniques.	10
Bibliography	15
CHAPTER 2. Fundamentals of interface and colloid science	21
2.1 Real and model dispersions.	22
2.2 Parameters of the model dispersion medium.	24
2.2.1 Gravimetric parameters.	25
2.2.2 Rheological parameters.	25
2.2.3 Acoustic parameters.	26
2.2.4 Thermodynamic parameters.	27
2.2.5 Electrodynamic parameters.	28
2.2.6 Electroacoustic parameters.	29
2.2.7 Chemical composition.	30
2.3 Parameters of the model dispersed phase.	31
2.3.1 Rigid vs. soft particles.	33
2.3.2 Particle size distribution.	34
2.4. Parameters of the model interfacial layer.	39
2.4.1. Flat surfaces.	41
2.4.2 Spherical DL, isolated and overlapped.	42
2.4.3 Electric Double Layer at high ionic strength.	45
2.4.4 Polarized state of the Electric Double Layer	47
2.5. Interactions in Colloid and Interface science	50
2.5.1. Interactions of colloid particles in equilibrium. Colloid stability	51
2.5.2 Interaction in a hydrodynamic field. Cell and core-shell models. Rheology.	55
2.5.3 Linear interaction in an electric field. Electrokinetics and dielectric spectroscopy.	62
2.5.4 Non-linear interaction in the electric field. Electrocoagulation and electro-rheology.	68
2.6. Traditional particle sizing.	73

2.6.1 Light Scattering. Extinction=scattering+absorption.	74
Bibliography	80
CHAPTER 3. Fundamentals of acoustics in liquids	89
3.1. Longitudinal waves and the wave equation.	89
3.2. Acoustics and its relation to Rheology.	92
3.3. Acoustic Impedance.	98
3.4 Propagation through phase boundaries - Reflection.	100
3.5 Propagation in porous media.	102
3.6 Chemical composition influence.	105
Bibliography	112
CHAPTER 4. Acoustic theory for particulates	119
4.1 Extinction=absorption + scattering. Superposition approach.	122
4.2 Acoustic theory for a dilute system.	133
4.3 Ultrasound absorption in concentrates.	137
4.3.1 Coupled phase model.	138
4.3.2 Viscous losses theory.	143
4.3.3 Thermal losses theory.	147
4.3.4 Structural loss theory.	152
4.3.5 Intrinsic loss theory.	156
4.4. Ultrasound scattering	157
4.4.1 Rigid sphere.	163
4.4.2 Rigid Cylinder.	164
4.4.3 Non-rigid sphere.	165
4.4.4 Porous sphere.	166
4.4.5 Scattering by a group of particles.	167
4.4.6 Ultrasound resonance by bubbles.	168
4.5 Input parameters.	169
Bibliography	174
CHAPTER 5. Electroacoustic theory	179
5.1 The Theory of Ion Vibration Potential (IVP).	183
5.2 The Low frequency electroacoustic limit - Smoluchowski limit, (SDEL).	185
5.3 The O'Brien theory.	187
5.4 The Colloid Vibration Current in concentrated systems.	191
5.4.1 CVI and Sedimentation Current.	193
5.4.2 CVI for polydisperse systems.	198
5.4.3 Surface conductivity.	200
5.4.4 Maxwell-Wagner relaxation. Extended frequency range.	201
5.5 Qualitative analysis.	202
Bibliography	205
CHAPTER 6. Experimental verification of the acoustic and electroacoustic theories	211
6.1 Viscous losses.	211
6.2 Thermal losses.	217
6.3 Structural losses.	219
6.4 Scattering losses.	223
6.5 Electroacoustic phenomena.	227
Bibliography	232
CHAPTER 7. Acoustic and electroacoustic measurement techniques	237
7.1 Historical Perspective.	237
7.2 Difference between measurement and analysis.	238
7.3 Measurement of attenuation and sound speed using Interferometry.	239
7.4 Measurement of attenuation and sound speed using the transmission technique.	240
7.4.1 Historical development of the transmission technique.	240

7.4.2 Detailed Description of the Dispersion Technology DT-100 Acoustic Spectrometer.	243
7.5 Precision, accuracy, and dynamic range for transmission measurements.	253
7.6 Analysis of Attenuation and Sound Speed to yield desired outputs.	257
7.6.1 The ill-defined problem.	257
7.6.2 Precision, accuracy, and resolution of the analysis.	263
7.7 Measurement of Electroacoustic properties.	268
7.7.1 Electroacoustic measurement of CVI.	268
7.7.2 CVI measurement using energy loss approach.	271
7.8 Zeta potential calculation from the analysis of CVI.	274
7.9 Measurement of acoustic Impedance.	275
Bibliography	278
CHAPTER 8. Applications of acoustics for characterizing particulate systems	283
8.1 Characterization of aggregation and flocculation.	283
8.2 Stability of emulsions and microemulsions.	293
8.3 Particle sizing in mixed colloids with several dispersed phases.	301
8.3.1 High density contrast - Ceramics, oxides, minerals, pigments.	304
8.3.2 Cosmetics - Sunscreen.	317
8.3.3 Composition of mixtures.	321
8.4. Chemical-mechanical polishing. Large particle resolution.	326
8.5. Titration using Electroacoustics.	336
8.5.1 pH titration.	336
8.5.2 Time titration, kinetic of the surface-bulk equilibration.	338
8.5.3 Surfactant titration.	339
8.6. Colloids with high ionic strength - Electroacoustic background.	344
8.7 Effect of air bubbles.	351
8.8 Table of Applications.	352
Bibliography	360
List of symbols	373
Bibliography alphabetical	381
Index	419

Chapter 1. Introduction

Two key words define the scope of this book: “ultrasound” and “colloids”. In turn, each word is a key to a major scientific discipline, Acoustics on one hand and Colloid Science on the other. It is a rather curious situation that, historically, there has been little real communication between disciples of these two fields. Although there is a large body of literature devoted to ultrasound phenomena in colloids, mostly from the perspective of scientists from the field of Acoustics, there is little recognition that such phenomena may be of real importance for both the development, and application, of Colloid Science. From the other side, colloid scientists have not embraced acoustics as an important tool for characterizing colloids. The lack of any serious dialog between these scientific fields is perhaps best illustrated by the fact that there are no references to ultrasound or Acoustics in the major handbooks on Colloid and Interface Science [1,2] nor any reference to colloids in handbooks on acoustics [3,4,5].

One might ask “Perhaps this link does not exist because it is not important to either discipline?” In order to answer this question, let us consider the potential place of Acoustics within an overall framework of Colloid Science. For this purpose, it is helpful to classify non-equilibrium colloidal phenomena in two dimensions; the first determined by whether the relevant disturbances are electrical, mechanical, or electro-mechanical in nature and the second based on whether the time domain of that disturbance can be described as stationary, low frequency, or high frequency. Table 1.1 illustrates this classification of major colloidal

phenomena. The low and high frequency ranges are separated based on the relationship between either the electric or mechanical wavelength λ , and some system dimension L . Clearly, light scattering represents electrical phenomena in colloids at high frequency (the wavelength of light is certainly smaller than the system dimension). There was, however, no mention in colloid textbooks, until very recently, of any mechanical or electro-mechanical phenomena in the region where the mechanical or electrical wavelength is shorter than the system dimension. This would appear to leave two empty spaces in Table 1.1. Such mechanical wavelengths are produced by “Sound” or, when the frequency exceeds our hearing limit of 20 KHz, by “Ultrasound”. For reference, ultrasound wavelengths lie in the range from 10 microns to 1 mm, whereas the system dimension is usually in the range of centimeters. For this reason, we consider ultrasound related effects to lie within the high frequency range. One of the empty spaces can be filled by acoustic measurements at ultrasound frequencies, which characterize colloidal phenomena of a mechanical nature at high frequency. The second empty space can be filled by electroacoustic measurements, which allow us to characterize electro-mechanical phenomena at high frequency. This book will help fill these gaps and demonstrate that acoustics (and electroacoustics) and can bring much useful knowledge to Colloid Science. As an aside, we do not consider here the use of high power ultrasound for modifying colloidal systems, just the use of low power sound as a non-invasive investigation tool that has very unique capabilities.

Table 1.1 Colloidal phenomena

	Electrical nature	Electro-mechanical	Mechanical nature
Stationary	Conductivity, Surface conductivity.	Electrophoresis, Electroosmosis, Sedimentation potential, Streaming current/potential, Electro-viscosity	Viscosity, Stationary colloidal hydrodynamics, Osmosis, Capillary flow.
Low frequency ($\lambda > L$)	Dielectric spectroscopy.	Electro-rotation, Dielectrophoresis.	Oscillatory rheology.
High frequency ($\lambda < L$)	Optical scattering, X-ray spectroscopy.	Empty? Electroacoustics!	Empty? Acoustics!

There are several questions that one might ask when starting to read this book. We think it is important to deal with these questions right away, at least giving some preliminary answers, which will then be clarified and expanded later in the main text. Here are these questions and the short answers.

Why should one care about Acoustics if generations of colloid scientists worked successfully without it?

While it may be true at present that the usefulness of Acoustics is not widely understood, it seems that earlier generations had a somewhat better appreciation. Many well-known scientists applied Acoustics to colloidal systems, as will be described in a detailed historical overview in the next section. Briefly, we can mention the names of Stokes, Rayleigh, Maxwell, Henry, Tyndall, Reynolds, and Debye, all of whom considered acoustic phenomena in colloids as deserving of their attention. The first colloid-related acoustic effect to be studied was the propagation of sound through fog; contributions by Henry, Tyndall and Reynolds made more than century ago between 1870-80. Another interesting, but not so well known fact, is that Lord Rayleigh, the first author of a scattering theory, entitled his major books “Theory of Sound”. He developed the mathematics of scattering theory mostly for sound, not for light as is often assumed by those not so familiar with the history of Colloid Science. In fact, the main reference to light in his work was a paragraph or two on “why the sky is blue”.

If Acoustics is so important why has it remained almost unknown in Colloid Science for such a long time?

We think that the failure to exploit acoustic methods might be explained by a combination of factors: the advent of the laser as a convenient source of monochromatic light, technical problems with generating monochromatic sound beams within a wide frequency range, the mathematical complexity of the theory, and complex statistical analysis of the raw data. In addition, acoustics is more dependent on mathematical calculations than other traditional instrumental techniques. Many of these problems have now been solved

mostly due to the advent of fast computers and the development of new theoretical approaches. As a result there are a number commercially available instruments utilizing ultrasound for characterizing colloids, produced by Matec, Malvern, Sympatec, Colloidal Dynamics, and Dispersion Technology.

What information does ultrasound based instruments yield?

For colloidal systems, ultrasound provides information on the three important areas of particle characterization: Particle sizing, Rheology, and Electrokinetics.

In addition ultrasound can be used as a tool for characterizing properties of pure liquids and dissolved species like ions or molecules, but we will cover this aspect only briefly.

An Acoustic spectrometer may measure the attenuation of ultrasound, the propagation velocity of this sound, and/or the acoustic impedance, in any combination depending on the instrument design. The measured acoustic properties contain information about the particle size distribution, volume fraction, as well as structural and thermodynamic properties of the colloid. One can extract this information by applying the appropriate theory in combination with a certain set of *a priori* known parameters. Hence, an Acoustic spectrometer is not simply a particle-sizing instrument. By applying sound we apply stress to the colloid and consequently the response can be interpreted in rheological terms, as will be shown below. In addition to acoustics there is one more ultrasound-based technique, which is called Electroacoustics. The Electroacoustic phenomenon, first predicted by Debye in 1933, results from coupling between acoustic and electric fields. There are two ways to produce such an Electroacoustic phenomenon depending on which field is the driving force. When the driving force is the electric field and we observe an acoustic response we speak of ElectroSonic Amplitude (ESA). Alternatively, when the driving force is the acoustic wave we speak, instead, of the Colloid Vibration Potential (CVP) if we observe an open circuit potential, or a Colloid Vibration Current (CVI) if we observe a short circuit current. Such electroacoustic techniques yield information about the electrical properties of colloids. In principle, it can also be used for particle sizing.

Where can one apply ultrasound?

The following list gives some idea of the existing applications for which the ultrasound based characterization technique is appropriate:

Aggregative stability, Cement slurries, Ceramics, Chemical-Mechanical Polishing, Coal slurries, Coatings, Cosmetic emulsions, Environmental protection, Flotation, Ore enrichment, Food products, Latex, Emulsions and micro emulsions, Mixed dispersions, Nanosized dispersions, Non-aqueous dispersions, Paints, Photo Materials.

This list is not complete. A table in Chapter 8 summarizes all experimental works currently known to us.

What are the advantages of ultrasound over traditional characterization techniques?

There are so many advantages of ultrasound. The last section of this chapter is devoted to describing the relationship between ultrasound based and traditional colloidal characterization techniques.

Finally, we would like to stress that this book targets primarily scientists who consider colloids as their major object of interest. As such we emphasize those aspects of acoustics that are important for colloids and, thereby, neglect many others.

On the other hand, scientist working with ultrasound will already be familiar with many of the theoretical and experimental developments presented in this book. At the same time they will find several important new developments. In particular we would like to mention:

- a general approach to acoustics in colloids by combination of ultrasound absorption and ultrasound scattering;
- a general solution for eliminating multiple scattering;
- a theory of ultrasound absorption in concentrated systems;
- an electroacoustic theory for concentrates;
- experimental verification of these theories for concentrated systems;
- multiple existing applications.

1.1 Historical overview

The roots of our current understanding of sound go back more than 300 years to the first theory for calculating sound speed suggested by Newton [6]. Newton's work is still interesting for us today because it illustrates the importance of thermodynamic considerations in trying to adequately describe ultrasound phenomena. Newton assumed that sound propagates while maintaining a constant temperature, i.e. an isothermal case. Laplace later corrected this misunderstanding by showing that it was actually adiabatic in nature [6].

This thermodynamic aspect of sound provides a good example of the importance of keeping a historical perspective. At least twice during the past 200 years the thermodynamic contribution to various sound-related phenomena was initially neglected, and only later found to be quite important. This thermodynamic neglect happened first in the 19th century, when Stokes's purely hydrodynamic theory for sound attenuation [9, 10] was later corrected by Kirchhoff [7, 8]. Then again, in the 20th century, Sewell's hydrodynamic theory for sound absorption in heterogeneous media [12] was later extended by Isakovich [11] by the introduction of a mechanism for thermal losses.

We have now a very similar situation concerning electroacoustics. Until quite recently all such theories neglected any thermodynamic contribution [13, 14, 15, 16, and 17]. Based on historical perspective, we might reasonably inquire about the potential importance of thermodynamic considerations for electroacoustics. Shilov and others [18] have addressed this query and revealed a new interesting feature of the electroacoustic effect.

Table 1.2 lists important steps in the development of our understanding of sound. From the very beginning sound was considered as a rather simple example that allowed development of a general theory of "wave" phenomena. Then, later, the new understanding achieved for sound was extended to other wave phenomena, such as light. Tyndall, for example, used reference to sound to explain the wave nature of the light [19, 20]. Newton's Corpuscular Theory of Light was first opposed both by the celebrated astronomer Huygens and the, no less celebrated, mathematician Euler. They each held that light, like *sound*, was a product of wave-motion. In the case of *sound*, the velocity depends upon the relation of elasticity to density in the body that transmits the sound. The greater the elasticity the greater is the velocity, and the less the density the greater is the velocity. To account for the enormous velocity of propagation in the case of light, the substance that transmits it is assumed to have both extreme elasticity and extreme density.

This dominance of sound over light as examples of the wave phenomena continued even with Lord Rayleigh, who developed his theory of scattering mostly for sound and paid much less attention to light [6,21-24]. At the end of the 19th century sound and light parted because further investigation was directed more on the physical roots of the each phenomenon instead on their common wave nature.

The history of light and sound in Colloid Science is very different. Light has been an important tool since the first microscopic observations of Brownian motion and the first electrophoretic measurements. It became even more important in middle of the 20th century through the use of light scattering for the determination of particle size.

In contrast, sound remained unknown in Colloid Science despite a considerable amount of work in the field of Acoustics using fluids that were essentially of a colloidal nature. The goal of these studies was to learn more about Acoustics, but not about colloids. This is the spirit in which the ECAH theory (Epstein-Carhart-Allegra-Hawley [25, 26]), for ultrasound propagation through dilute colloids, was developed.

Although Acoustics was not used specifically for colloids, it was a powerful tool for other purposes. For instance, it was used to learn more about the structure of pure liquids and the nature of chemical reactions in liquids. These studies, associated with the name of Prof. Eigen, who received a Nobel Prize in 1968 [27-29], are described in more detail in the chapter "Fundamentals of Acoustics".

It is curious that the penetration of ultrasound into Colloid Science began with electroacoustics, which is more complex than traditional acoustics. An Electroacoustic effect was predicted for ions by Debye in 1933 [30] and later extended to colloids by Hermans and, independently, Rutgers in 1938 [31]. The early experimental electroacoustic work is associated with Yeager and Zana, who conducted many experiments in the 1950's and 60's with various co-authors [32-35]. Later this work was continued by Marlow, O'Brien, Ohshima, Shilov, and the authors of this book [13, 15, 16, 17, 18, 36, and 37]. As a result, there are now several commercially available electroacoustic instruments for characterizing ζ -potential.

Acoustics only reached some recognition in the field of colloid science very recently. It was first suggested as a particle sizing tool by Cushman and others [77] in 1973, and later refined by Uusitalo and others [77], and for large particles by Riebel [38]. Development as a commercial instrument having the capability to measure a wide particle size range, was begun by Goetz, A.Dukhin, and Pendse in the 90's [39, 40, 41,42]. At the same time a group of British scientists, including McClements, Powey, and others [43, 44, 45, 46, 47, and 48], actively promoted it, especially for emulsions. There are now four commercially available acoustic spectrometers, manufactured by Malvern, Sympatec, Matec, and Dispersion Technology.

To conclude this short historical review we would like to mention a development that we consider of great importance for the future, namely the combination of both acoustic and electroacoustic spectroscopies. The synergism of this combination is described in papers and patents by A.Dukhin and P.Goetz [17, 37, 40, 41, 42, 49, 50, 72, and 73].

Table 1.2 Key Steps in understanding Sound related to Colloids.

Year	Author	Topic
1687	Newton [6]	Sound speed in fluid, theory, erroneous isothermal assumption
Early 1800's	Laplace [6]	Sound speed in fluid, theory, adiabatic assumption
1820	Poisson [51,52]	Scattering by atmosphere arbitrary disturbance, first successful theory
1808	Poisson [51,52]	Reflection from rigid plane, general problem
1845-1851	Stokes [9,10]	Sound attenuation in fluid, theory, viscous losses
1842	Doppler [53]	Alternation of pitch by relative motion
1868	Kirchhoff [7,8]	Sound attenuation in fluid, theory, thermal losses
1866	Maxwell [54]	Kinetic theory of viscosity
1870-80	Henry, Tyndall, Reynolds [19,20,55,56]	First application to colloids - sound propagation in fog
1871	Rayleigh [21,22]	Scattering of light by small particles
1875-80	Rayleigh [6,23,24]	Diffraction and scattering of sound, Fresnel zones in Acoustics
1878	Rayleigh [6]	Theory of Sound, Vol. II
1910	Sewell [12]	Viscous attenuation in colloids, theory
1933	Debye [30]	Electroacoustic effect, introduction for ions
1936	Morse [3]	Scattering theory for arbitrary wavelength-size ratio
1938	Hermans [31]	Electroacoustic effect, introduced for colloids
1944	Foldy [57,58]	Acoustic theory for bubbles
1948	Isakovich [11]	Thermal attenuation in colloids, theory
1946	Pellam, Galt [59]	Pulse technique
1947	Bugosh, Yaeger [32]	Electroacoustic theory for electrolytes
1951-3	Yeager, Hovorka, Derouet, Denizot [33-35,60]	First electroacoustic measurements
1951-2	Enderby, Booth [61-62]	First electroacoustic theory for colloids
1953	Epstein and Carhart [25]	General theory of sound attenuation in dilute colloids
1958-9	Happel, Kuwabara [63-65]	Hydrodynamic cell models
1962	Andreae et al [66,67]	Multiple frequencies attenuation measurement
1967	Eigen et al [27-28]	Nobel price, acoustics for chemical reactions in liquids
1972	Allegra and Hawley [26]	Finalized ECAH theory for dilute colloids
1973	Cushman [77]	First patent for acoustic particle sizing
1974	Levine, Neale [68]	Electrokinetic cell model
1978	Beck [36]	Measurement of ζ -potential by ultrasonic waves
1981	Shilov and Zharkikh [69]	Corrected electrokinetic cell model
1983	Marlow, Fairhurst, Pendse [36]	First electroacoustic theory for concentrates
1983	Uusitalo [76]	Mean particle size from acoustics, patent
1983	Oja, Peterson, Cannon [70]	ESA electroacoustic effect
1988	Harker, Temple [71]	Coupled phase model for acoustics of concentrates
1987	Riebel [38]	Particle size distribution, patent for the large particles
1988-9	O'Brien [13,15]	Electroacoustic theory, particle size and ζ -potential from electroacoustics

1990	Anson, Chivers [47]	Materials database
1999	Shilov and others [16,17]	Electroacoustic theory for CVI in concentrates
1990 to present	McClements, Povey [43,44,45]	Acoustics for emulsions
1996 to present	A.Dukhin, P.Goetz [39,72,73]	Combining together acoustics and electroacoustics for Particle sizing, Rheology and Electrokinetics

1.2 Advantages of ultrasound over traditional characterization techniques

There is one major advantage of ultrasound-based techniques compared to traditional characterization methods. Ultrasound can propagate through concentrated suspensions and consequently allows one to characterize concentrated dispersions as is, without any dilution. This feature of ultrasound is applicable to both particle size and ζ -potential measurement. Dilution required by traditional techniques can destroy aggregates or flocs and the corresponding measured particle size distribution for that dilute system would not be correct for the concentrate.

Elimination of dilution is especially critical for ζ -potential characterization because this parameter is a property of both the particle and the surrounding liquid; dilution changes the suspension medium and, as a result, ζ -potential.

The many advantages of ultrasound for characterizing particle size are summarized in Table 1.3. Detailed analysis of the ultrasound-based techniques is given later in this book. The following is a short summary. Acoustic methods are very robust and precise [72,73]. They are much less sensitive to contamination compared to the traditional light-based techniques because the high concentration of particles in the fresh sample dominates any small residue from the previous sample. It is a relatively fast technique. Normally a single particle size measurement can be completed in a few minutes. This feature, together with the ability to measure flowing systems, makes acoustic attenuation very attractive for monitoring particle size on-line.

Table 1.3 Features and benefits of acoustics over traditional particle sizing techniques.

Feature	Benefit
No dilution required.	Less sensitive to contamination
No calibration with the known particle size	More accurate
Particle size range from 5 nm to 1000 microns with the same sensor.	Simpler hardware, more cost effective
Simple decoupling of sound adsorption and sound scattering	Simplifies theory
Possible to eliminate multiple scattering even at high volume fractions up to 50%vol	Simplifies theory for large particle size
Existing theory for ultrasound absorption in concentrates with particles interaction	Possible to treat small particles in concentrates
Data available over wide range of wavelength	Allows use of simplified theory and reduces particle shape effects
Innate weight basis, lower power of the particle size dependence	Better for polydisperse systems
Particle sizing in dispersions with several dispersed phases (mixed dispersions)	Real world, practical systems
Particle sizing in structured dispersions.	

There are several advantages of ultrasound over light based instruments because of the longer wavelength used. The wavelength of ultrasound in water at the highest frequency typically used (100 MHz) is about 15 microns and it increases even further to 1.5 millimeter at the lowest frequency (1 MHz). In contrast light based instruments typically use wavelengths on the order of 0.5 microns. If the particles are small compared to the wavelength we say that this satisfies the Rayleigh long wavelength requirement. It is known that particle sizing in this long wavelength range is more desirable than in the intermediate or short wave length range because of lower sensitivity to shape factors and also a simpler theoretical interpretation. As a result, using the longer wavelengths available through acoustics allows us to characterize a much wider range of particle size while still meeting this long wavelength requirement. Nature provided one more significant advantage of ultrasound over light, and that is related to the wavelength dependence. As the wave travels through the colloid, it is known that the extinction of both ultrasound and light occurs due to the combined effects of both scattering and absorption [3, 74]. Since most light scattering experiments are performed at a single wavelength it is not possible to experimentally separate these two contributions to the total extinction. In fact, more often than not, the absorption of light is simply neglected in most light scattering experiments, and this can lead to errors.

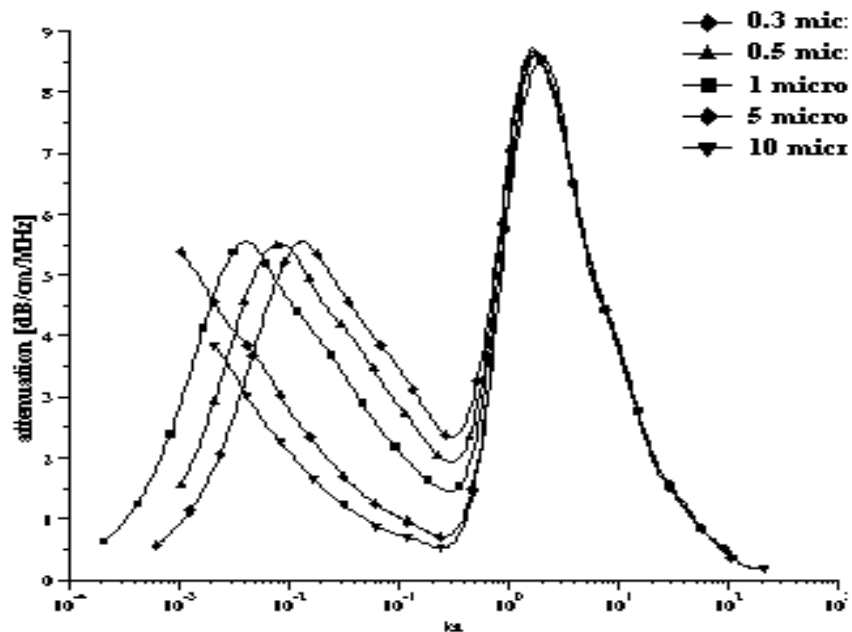


Figure 1.1 Scattering attenuation and viscous absorption of ultrasound.

In the case of ultrasound, the absorption and scattering are distinctively separated on the wavelength scale. Figure 1.1 illustrates the dependence of ultrasound attenuation as a function of relative wavelength ka defined by:

$$ka = \frac{2\pi a}{\lambda} \quad (1.1)$$

where a is the particle radius and λ is the wavelength of ultrasound.

It is seen that attenuation curve has two prominent ranges. The low frequency region corresponds to the absorption; the higher frequency region corresponds to the scattering. It is obvious from inspection of

Figure 1.1 that it is a simple matter to separate both contributions because there is very little, indeed almost negligible overlap.

This peculiar aspect of ultrasound frequency dependence allows one to simplify the theory tremendously. Indeed, in the wide majority of cases absorption and scattering can be considered separately. This simplification is valid except for very high volume fractions and for some special non-aqueous systems with soft particles [75].

Electroacoustics is a relatively new technique compared to acoustics. In principle it can provide information for both particle sizing and ζ -potential characterization. However, we believe that acoustics is much more suited to particle sizing than electroacoustics. For this reason, justified later in Chapters 4,5, and 7, we consider electroacoustics as primarily a technique for characterizing only the electric surface properties like ζ -potential. In this sense electroacoustics competes with microelectrophoresis and other traditional electrokinetic methods. However, electroacoustics has many advantages over traditional electrokinetic methods that can be summarized as:

- no dilution required, volume fraction up to 50%v/v;
- less sensitive to contamination; easier to clean;
- higher precision (± 0.1 mV);
- low surface charges (down to 0.1 mV);
- electrosmotic flow is not important;
- convection is not important;
- faster.

In addition, electroacoustic probes can be used for various titration experiments, as it will be shown later in Chapter 8.

The third field where ultrasound competes with traditional colloid characterization is the field of rheology. This is relatively new area of ultrasound application. We can count two obvious advantages of ultrasound over traditional rheometers. First, ultrasound measurements are non-destructive and allow us to obtain information about the high frequency rheological properties while keeping the sample intact. The second advantage is related to the ability to characterize volume viscosity in addition to the shear viscosity. This was already known to Stokes 150 years ago [9]. Volume viscosity is a more sensitive probe of any structural features in a system but it is impossible to measure using shear-based techniques. Ultrasound attenuation is the only known technique able to characterize this important rheological parameter. This aspect will be dealt with in detail later in Chapter 3.

In conclusion, we think that the combination of acoustics and electroacoustics enhances each of them [39]. In addition, there is certain overlap in their nature that offers a way to create various consistency tests to verify the reliability of the data.

Bibliography

1. Lyklema, J. "Fundamentals of Interface and Colloid Science", Volumes 1, Academic Press, (1993)
2. Hunter, R.J. "Foundations of Colloid Science", Oxford University Press, Oxford, (1989)
3. Morse, P. and Ingard, U. "Theoretical Acoustics", McGraw-Hill, NY, (1968)
4. Kinsler, L., Frey, A., Coppens, A. and Sanders, J. "Fundamentals of Acoustics", J. Wiley & Sons, NY, (2000)
5. Blackstock, D. "Fundamentals of Physical Acoustics", J. Wiley & Sons, NY, (2000)
6. Rayleigh, L. "The Theory of Sound", Vol.2, Macmillan and Co., NY, second edition 1896, first edition (1878).
7. Kirchhoff, Pogg. Ann., vol. CXXXIV, p.177, (1868)
8. Kirchhoff, "Vorlesungen uber Mathematische Physik", (1876)
9. Stokes, "On a difficulty in the Theory of Sound", Phil. Mag., Nov. (1848)
10. Stokes, "Dynamic Theory of Diffraction", Camb. Phil. Trans., IX, (1849)
11. Isakovich, M.A. Zh. Experimental and Theoretical Physics, 18, 907 (1948)
12. Sewell, C.T.J., "The extinction of sound in a viscous atmosphere by small obstacles of cylindrical and spherical form", PhilTrans. Roy. Soc., London, 210, 239-270 (1910)
13. O'Brien, R.W. "Electro-acoustic Effects in a dilute Suspension of Spherical Particles", J. Fluid Mech., 190, 71-86 (1988)
14. Hunter, R.J. "Review. Recent developments in the electroacoustic characterization of colloidal suspensions and emulsions", Colloids and Surfaces, 141, 37-65 (1998)

15. O'Brien, R.W. "Determination of Particle Size and Electric Charge", US Patent 5,059,909, Oct.22, (1991)
16. Dukhin, A.S., Shilov, V.N., Ohshima, H., Goetz, P.J "Electroacoustics Phenomena in Concentrated Dispersions. New Theory and CVI Experiment", *Langmuir*, 15, 20, 6692-6706, (1999)
17. Dukhin, A.S., Shilov, V.N., Ohshima, H., Goetz, P.J "Electroacoustics Phenomena in Concentrated Dispersions. Effect of the Surface Conductivity", *Langmuir*, 16, 2615-2620 (2000)
18. Shilov, V.N. and Dukhin A.S. "Sound-induced thermophoresis and thermodiffusion in electric double layer of disperse particles and electroacoustics of concentrated colloids." *Langmuir*, submitted.
19. Tyndall, J. "Light and Electricity", D. Appleton and Com., NY (1873).
20. Tyndall, J. "Sound", *Phil. Trans.*, 3rd addition, (1874)
21. Rayleigh, J.W. "On the Light from the Sky", *Phil. Mag.*, (1871)
22. Rayleigh, J.W. "On the scattering of Light by small particles", *Phil. Mag.*, (1871)
23. Rayleigh, J.W. "Acoustical Observations", *Phil. Mag.*, vol IX, p. 281, (1880)
24. Rayleigh, J.W. "On the Application of the Principle of Reciprocity to Acoustics", *Royal Society Proceedings*, vol XXV, p. 118, (1876)
25. Epstein, P.S. and Carhart R.R., "The Absorption of Sound in Suspensions and Emulsions", *J. of Acoust. Soc. Amer.*, 25, 3, 553-565 (1953)
26. Allegra, J.R. and Hawley, S.A. "Attenuation of Sound in Suspensions and Emulsions: Theory and Experiments", *J. Acoust. Soc. Amer.*, 51, 1545-1564 (1972)
27. Eigen., "Determination of general and specific ionic interactions in solution", *Faraday Soc. Discussions*, , No.24, p.25 (1957)
28. Eigen, M. and deMaeyer, L. in "Techniques of Organic Chemistry", (ed. Weissberger) Vol. VIII Part 2, Wiley (1963)
29. DeMaeyer, L., Eigen, M., and Suarez, J. "Dielectric Dispersion and Chemical Relaxation", *J. Of the Amer. Chem. Soc.*, 90, 12, 3157-3161(1968)
30. Debye, P. *J. Chem. Phys.*, 1, 13 (1933)
31. Hermans, J. *Philos. Mag.*, 25, 426 (1938)
32. Bugosh, J., Yeager, E. and Hovorka, F. *J. Chem. Phys.* 15, 592 (1947)
33. Yeager, E. and Hovorka, F. *J. Acoust. Soc. Amer.*, 25, 443 (1953)
34. Yeager, E., Dietrick, H. and Hovorka, F. *J. Acoust. Soc. Amer.*, 25, 456 (1953)
35. Zana, R. and Yeager, E. *J. Phys. Chem*, 71, 4241 (1967)
36. Beck et al., "Measuring Zeta Potential by Ultrasonic Waves", *Tappi*, vol.61, 63-65, (1978)
37. Dukhin, A.S., Shilov, V.N. and Borkovskaya, Yu. "Dynamic Electrophoretic Mobility in Concentrated Dispersed Systems. Cell Model.", *Langmuir*, 15, 10, 3452-3457 (1999)
38. Riebel, U. et al. "The Fundamentals of Particle Size Analysis by Means of Ultrasonic Spectrometry" *Part. Part. Syst. Charact.*, vol.6, pp.135-143, (1989)
39. Dukhin, A.S. and Goetz, P.J. "Acoustic and Electroacoustic Spectroscopy", *Langmuir*, 12, 19, 4336-4344 (1996)
40. Dukhin, A.S. and Goetz, P.J. "Characterization of aggregation phenomena by means of acoustic and electroacoustic spectroscopy", *Colloids and Surfaces*, 144, 49-58 (1998)
41. Dukhin, A.S. and Goetz, P.J. "Method and device for characterizing particle size distribution and zeta potential in concentrated system by means of Acoustic and Electroacoustic Spectroscopy", patent USA, 09/108,072, (2000)
42. Dukhin, A.S. and Goetz, P.J. "Method and device for Determining Particle Size Distribution and Zeta Potential in Concentrated Dispersions", patent USA, pending
43. Povey, M. "The Application of Acoustics to the Characterization of Particulate Suspensions", in *Ultrasonic and Dielectric Characterization Techniques for Suspended Particulates*, ed. V. Hackley and J. Texter, Am. Ceramic Soc., Ohio, (1998)
44. McClements, J.D. "Ultrasonic Determination of Depletion Flocculation in Oil-in-Water Emulsions Containing a Non-Ionic Surfactant", *Colloids and Surfaces*, 90, 25-35 (1994)
45. McClements, D.J. "Comparison of Multiple Scattering Theories with Experimental Measurements in Emulsions" *The Journal of the Acoustical Society of America*, vol.91, 2, pp. 849-854, February (1992)
46. Holmes, A.K., Challis, R.E. and Wedlock, D.J. "A Wide-Bandwidth Study of Ultrasound Velocity and Attenuation in Suspensions: Comparison of Theory with Experimental Measurements", *J. Colloid and Interface Sci.*, 156, 261-269 (1993)

47. Anson, L.W. and Chivers, R.C. "Thermal effects in the attenuation of ultrasound in dilute suspensions for low values of acoustic radius", *Ultrasonic*, 28, 16-25 (1990)
48. Holmes, A.K., Challis, R.E. and Wedlock, D.J. "A Wide-Bandwidth Ultrasonic Study of Suspensions: The Variation of Velocity and Attenuation with Particle Size", *J. Colloid and Interface Sci.*, 168, 339-348 (1994)
49. Dukhin, A.S. and Goetz, P.J. "Acoustic Spectroscopy for Concentrated Polydisperse Colloids with High Density Contrast", *Langmuir*, 12, [21] 4987-4997 (1996)
50. Wines, T.H., Dukhin A.S. and Somasundaran, P. "Acoustic spectroscopy for characterizing heptane/water/AOT reverse microemulsion", *JCIS*, 216, 303-308 (1999)
51. Poisson, "Sur l'integration de quelques equations lineaires aux differnces prtielles, et particulierement de l'equation generalie du mouvement des fluides elastiques", *Mem., de l'Institut*, t.III, p.121, (1820)
52. Poisson, *Journal de l'ecole polytechnique*, t.VII, (1808)
53. Doppler, "Theorie des farbigen Lichtes der Doppelsterne", *Prag*, (1842)
54. Maxwell, "On the Viscosity or Internal Friction of Air and other Gases", *Phil. Trans.* vol 156, p.249, (1866)
55. Henry, Report of the Lighthouse Board of the United States for the year 1874.
56. Reynolds, O. *Proceedings of the Royal Society*, vol. XXII, p.531, (1874)
57. Foldy, L.L. "Propagation of sound through a liquid containing bubbles", *OSRD Report No.6.1-sr1130-1378*, (1944)
58. Carnstein, E.L. and Foldy, L.L. "Propagation of sound through a liquid containing bubbles", *J. of Acoustic Society of America*, 19, 3, 481- 499 (1947)
59. Pellam, J.R. and Galt, J.K. "Ultrasonic propagation in liquids: Application of pulse technique to velocity and absorption measurement at 15 Megacycles", *J. of Chemical Physics*, 14, 10 , 608-613 (1946)
60. Derouet, B. and Denizot, F. *C. R. Acad. Sci., Paris*, 233,368 (1951)
61. Booth, F. and Enderby, J. "On Electrical Effects due to Sound Waves in Colloidal Suspensions", *Proc. of Amer. Phys. Soc.*, 208A, 32 (1952)
62. Enderby, J.A. "On Electrical Effects Due to Sound Waves in Colloidal Suspensions", *Proc. Roy. Soc., London*, A207, 329-342 (1951)
63. Happel J. and Brenner, H, "Low Reynolds Number Hydrodynamics", *Martinus Nijhoff Publishers, Dordrecht, The Netherlands*, (1973)
64. Happel J., "Viscous flow in multiparticle systems:Slow motion of fluids relative to beds of spherical particles", *AICHE J.*, 4, 197-201 (1958)
65. Kuwabara, S. "The forces experienced by randomly distributed parallel circular cylinders or spheres in a viscous flow at small Reynolds numbers", *J. Phys. Soc. Japan*, 14, 527-532 (1959)
66. Andreae, J. and Joyce, P. "30 to 230 Megacycle Pulse Technique for Ultrasonic Absorption Measurements in Liquids", *Brit. J. Appl. Phys.*, v.13, p.462-467 (1962)
67. Andreae, J., Bass, R., Heasell, E., and Lamb, J. "Pulse Technique for Measuring Ultrasonic Absorption in Liquids", *Acustica*, v.8, p.131-142 (1958)
68. Levine, S. and Neale, G.H. "The Prediction of Electrokinetic Phenomena within Multiparticle Systems.I.Electrophoresis and Electroosmosis.", *J. of Colloid and Interface Sci.*, 47, 520-532 (1974)
69. Shilov, V.N., Zharkih, N.I. and Borkovskaya, Yu.B. "Theory of Nonequilibrium Electro-surface Phenomena in Concentrated Disperse System. I.Application of Nonequilibrium Thermodynamics to Cell Model.", *Colloid J.*, 43,3, 434-438 (1981)
70. Oja, T., Petersen, G. and Cannon, D. "Measurement of Electric-Kinetic Properties of a Solution", *US Patent 4,497,208*, (1985)
71. Harker, A.H. and Temple, J.A.G., "Velocity and Attenuation of Ultrasound in Suspensions of Particles in Fluids", *J.Phys.D.:Appl.Phys.*, 21, 1576-1588 (1988)
72. Dukhin, A.S. and Goetz, P.J. "Acoustic and Electroacoustic Spectroscopy for Characterizing Concentrated Dispersions and Emulsions", *Adv. In Colloid and Interface Sci.*, 92, 73-132 (2001)
73. Dukhin, A.S. and Goetz, P.J. "New Developments in Acoustic and Electroacoustic Spectroscopy for Characterizing Concentrated Dispersions", *Colloids and Surfaces*, 192, 267-306 (2001)
74. Bohren, C. and Huffman, D. "Absorption and Scattering of Light by Small Particles", *J. Wiley & Sons*, (1983)
75. Babick, F., Hinze, F. and Ripperger, S. "Dependence of Ultrasonic Attenuation on the Material Properties", *Colloids and Surfaces*, 172, 33-46 (2000)

76. Uusitalo, S.J., von Alftan, G.C., Andersson, T.S., Paukku, V.A., Kahara, L.S. and Kiuru, E.S. "Method and apparatus for determination of the average particle size in slurry", US Patent 4,412,451 (1983)
77. Cushman and oth. US Patent 3,779,070 (1973)

On the other side, colloid scientists have not embraced acoustics as an important tool for characterizing colloids. The lack of any serious dialogue between these scientific fields is the biggest motivation behind this book. Covers in detail this multidisciplinary field combining acoustics, electroacoustics, colloid science, analytical chemistry and rheology. Provides a bibliography with more than 1,000 references. Presents theories and their experimental verification, as well as analysis of the methods and hardware pertaining to applications such as pharmaceuticals, ceramics, and polymers.Â Books related to Characterization of Liquids, Nano- and Microparticulates, and Porous Bodies using Ultrasound. Skip this list. Ultrasound for Characterizing Colloids: Particle Sizing, Zeta Potential, Rheology. Andrei S. Dukhin and Philip J. Goetz (Eds.) Year: 2002.

Testing > In silico/Modeling. Using Ultrasound Scanning to Characterize Colloidal Particles. October 6, 2013 Contact Author Malcolm Povey, Procter Department of Food Science and Lyn S. Daintree, PhD, Institute of Particle Science & Engineering. Close. During flocculation, individual colloid particles move more closely together under the influence of osmotic forces that are a common cause of destabilization in modern colloidal preparations. For colloidal systems, ultrasound provides information on three important areas of particle characterization: Particle sizing, Rheology, and Electrokinetics. This book primarily targets scientists who consider colloids as their major object of interest. As such we emphasize those aspects of acoustics that are important for colloids, and thereby neglect many others. Two key words define the scope of this book: 'ultrasound' and 'colloids'. Historically, there has been little real communication between disciples of these two fields. Although there is a large body of literature devoted to ultrasound phenomenon in colloids, there is little recognition that such phenomena may be of real importance for both the development, and application, of Colloid Science. Ultrasound for Characterizing Colloids: Particle Sizing, Zeta Potential, Rheology. Andrei S. Dukhin and Philip J. Goetz (Eds.) Year: 2002.