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# ULTRASOUND FOR CHARACTERIZING COLLOIDS

## Particle Sizing, Zeta Potential, Rheology

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*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

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,<br>Surface conductivity. | Electrophoresis,<br>Electroosmosis,<br>Sedimentation potential,<br>Streaming current/potential,<br>Electro-viscosity | Viscosity,<br>Stationary colloidal hydrodynamics,<br>Osmosis,<br>Capillary flow. |
| **Low frequency (λ>L)** | Dielectric spectroscopy. | Electro-rotation,<br>Dielectrophoresis. | Oscillatory rheology. |
| **High frequency (λ<L)** | Optical scattering,<br>X-ray spectroscopy. | **Empty?**<br><br>**Electroacoustics!** | **Empty?**<br>**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 theses 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 $\zeta$-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 $\zeta$-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 $\zeta$-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.

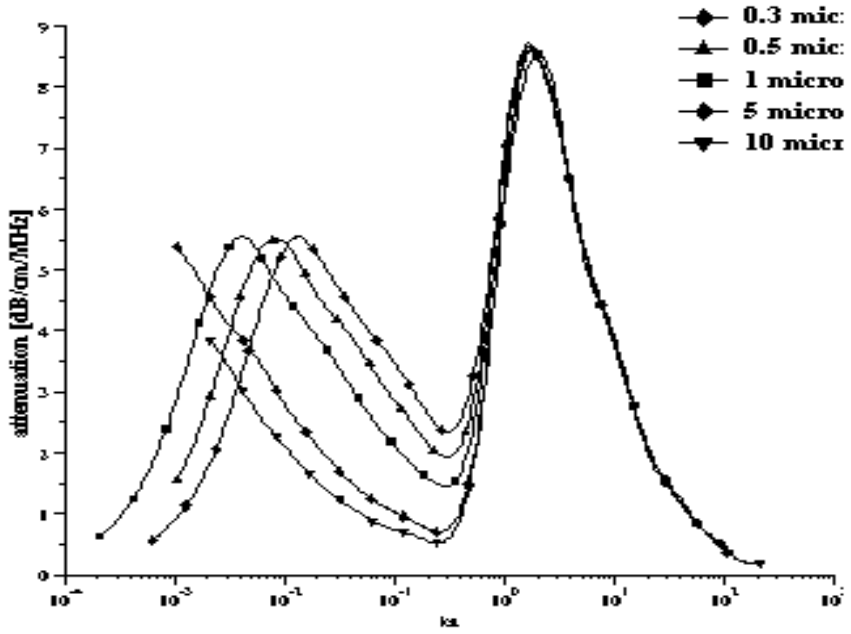


**Figure 1.1 Scattering attenuation and viscous absorption of ultrasound.**

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:

$$ka = \frac{2\pi a}{\lambda} \tag{1.1}$$

where $a$ is the particle radius and $\lambda$ 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%vl;
- 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.

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