

# Acoustic and Electroacoustic Spectroscopy

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Both acoustic and electroacoustic spectroscopy are related to a sound propagation through a heterogeneous system such as a suspension or an emulsion. An acoustic spectrometer measures only the changes in the properties of the sound wave, whereas an electroacoustic spectrometer deals with coupling between electrodynamic phenomena and the sound wave pressure field. Acoustic and electroacoustic spectroscopy are independent methods because the attenuation has little effect on the electroacoustic spectra and conversely electrokinetic phenomena have negligible effect on the attenuation spectra. Both techniques require a comprehensive theory to extract information about the particle size distribution or electrostatic parameters such as zeta potential from the measured spectra. The existing acoustic theory takes into account both compression and shear waves generated by oscillating particles. In contrast, the present theory for electroacoustics considers only shear waves. We will show that compression waves can also be important in electroacoustic phenomena. In fact, compression waves cause the dominant effect for conducting particles at the sufficiently low frequencies. As one would expect, each technique has advantages and disadvantages. Acoustic spectroscopy cannot give a complete characterization of the disperse system because it is able to characterize only particle size distribution. Electroacoustic spectroscopy, in certain cases, can provide a more complete characterization but requires assumptions about the sample which may not be valid, particularly in concentrated systems. A new approach is suggested here which combines acoustic and electroacoustic spectroscopy and eliminates the disadvantages of both.

## Introduction

Acoustic and electroacoustic spectroscopies are developing rapidly as an alternative to light scattering methods. The ability to characterize concentrated disperse systems provides much of the impetus for these developments.

Both techniques are based on well-established scientific background. For instance, McClements' review of acoustic spectroscopy<sup>1</sup> published in 1991 contains 127 references. This review classifies papers according to the measured parameters and the property of interest. Many new works related to acoustic and electroacoustic spectroscopies have appeared since that time. An updated version of McClements' classification is presented in Table 1. This table includes additional publications 51 related to both acoustic and electroacoustic spectroscopies. The publications already cited by McClements are prefixed by M, such as M.4.

In both methods, the interaction of sound with dispersed particles provides useful information. However, the set of measured parameters is different. In acoustic spectroscopy we measure attenuation and/or sound speed,<sup>1-21,74,75</sup> whereas for electroacoustic spectroscopy we measure either colloid vibration potential (CVP)<sup>22-29</sup> or electrostatic amplitude (ESA).<sup>30-50</sup> Electroacoustic spectroscopy requires also information about acoustic imped-

ance in order to calculate properly dynamic electrophoretic mobility. It means that there is some overlap between acoustic and electroacoustic measurements. This overlap

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**Table 1. References to Applications of Acoustic and Electroacoustic Spectroscopy to Emulsions and Suspensions**

property of interest	sound speed	measured parameters		
		attenuation	CVP	ESA
comparison with theory	M.4–M.15 2, 9, 12, 13, 14, 16, 18	M.5, M.10–M.21, M.24–M.35, M.54, M.59, M.68, M.69 9,12,13,16,18,74,75		
zeta potential			25–31	32–50, 69
particle size	M.14, M.15, M.47, M.66, M.90 2, 6, 7, 8, 14, 19, 20	M.14, M.47, M.50, M.53, M.90–M.94 6, 7, 8, 20, 74, 75		32, 33
volume fraction	M.15, M.36–M.47	M.8, M.15, M.36, M.38, M.40, M.47–M.53, M.55, M.56, M.58, M.63, M.70, 11		
creaming/sedimentation	M.60, M.64, M.71–M.75	M.65		
particle interaction	M.66, M.76–M.79 3, 5, 15	M.23, M.76, M.78, M.80–M.82 5, 15, 74, 75		
phase transition	M.22, M.57, M.61, M.62, M.66, M.77	M.23		

makes questionable the statement concerning acoustic and electroacoustic spectroscopes as independent methods. The detail consideration of this problem shows that overlap between acoustic and electroacoustic spectroscopy is not sufficient to provide the complete characterization of the system using only one from these two methods.

Each of these two independent types of dispersed system spectroscopies has advantages and disadvantages. We

believe that the combination of acoustic and electroacoustic spectroscopy can give a reliable and complete characterization of the concentrated disperse system. The justification for this statement is a subject of this paper.

Both, acoustic and electroacoustic spectroscopies require theory to interpret experimental data. The theory of the acoustic phenomena<sup>22,51–53</sup> takes into account the two types acoustic waves generated in the disperse system: compression and shear. Both types of the waves provide a significant contribution to the attenuation even at the relatively low frequencies when a wavelength exceeds a particle size. In contrast, the present theory of electroacoustics<sup>24,54</sup> neglects the contribution of the compression wave to the electroacoustic spectra. The reason and the validation of this difference between acoustic and electroacoustic phenomena are also subjects of this paper.

### Acoustic Spectroscopy

#### Attenuation, Sound Speed, and Acoustic Impedance for Characterizing Acoustic Spectroscopy.

Acoustic spectroscopy deals with the measurement of attenuation, sound speed, or acoustic impedance. The various types of the experimental technique (interferometry, pulse-echo overlap, Fourier transform pulse) are described in McClement's review.<sup>1</sup>

The sound attenuation coefficient  $\alpha$  is a convenient parameter characterizing total energy losses. It is equal to

$$\alpha = \frac{20 \log_{10} \frac{I_{\text{ini}}}{I_{\text{end}}}}{L} \frac{\text{db}}{\text{cm}} \quad (1)$$

where  $I_{\text{ini}}$  is initial sound intensity and  $I_{\text{end}}$  is the intensity after traveling a distance  $L$ . The ratio of sound intensities over some specific distance can be experimentally mea-

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sured. The computed value of  $\alpha$  reflects the total acoustic energy losses. This attenuation coefficient and the sound speed are the functions of the real and imaginary parts of a complex wave number  $\kappa$ . Thus

$$\alpha = -\text{Im}(\kappa) \quad (2)$$

$$V = \frac{\omega}{\text{Re}(\kappa)} \quad (3)$$

In acoustic spectroscopy we will speak mainly about the attenuation and sound speed. Nevertheless, it is convenient to define a complex acoustic impedance  $Z$  in order to compare acoustic and electroacoustic spectroscopy. This impedance is a ratio of the pressure in the acoustic wave to the velocity of the medium displacement. Acoustic impedance equals to:

$$Z = V\rho\left(1 - j\frac{V\alpha}{\omega}\right) = V\rho\left(1 - j\frac{\alpha\lambda}{2\pi}\right) \quad (4)$$

where  $j$  is  $\sqrt{-1}$ ,  $\omega$  is the sound frequency in radians/s, and  $\lambda$  is the wavelength of the sound.

The goal of acoustic spectroscopy is to determine the particle size distribution (PSD) of a dispersed system. Attenuation and sound speed spectra are the experimentally measured parameters. These spectra can be converted to particle size distribution (PSD) using theoretical model of the sound propagation through the dispersed system. This theoretical model should take into account multiple mechanisms of the sound interaction with the dispersed particles.

**Mechanisms of Sound Attenuation.** A sound wave interacts with the dispersed particles and to a lesser extent with the dispersion medium propagating through a colloid. As a result of this interaction, the properties of the sound wave change. A part of the acoustic energy fails to reach the receiving transducer. This part of the acoustic energy is dissipated by conversion to some other form of energy or diverted from the path between the transmitter and receiver transducers by scattering or other geometrical effects. Altogether, there are six known loss mechanisms produced by this interaction between the sound wave and the dispersed phase: (1) viscous losses; (2) thermal losses; (3) scattering losses; (4) intrinsic losses; (5) electrokinetic losses; (6) structural losses. Viscous, thermal, scattering, and intrinsic losses are included in most analyses of acoustic spectroscopy, whereas the electrokinetic and structural losses are either ignored or assumed to be negligibly small. However, structural losses can be quite significant, especially in concentrated systems. Nevertheless, spectroscopy based only on these first four mechanisms has been applied successfully for many real systems.

Acoustic spectroscopy is successful, first of all, in dilute systems. The theory of the sound propagation is well established only for dilute systems when particle-particle interaction is negligible weak. This theory has been in principle created by Epstein and Carhart<sup>51</sup> and then generalized for emulsions and suspensions by Allegra and Hawley.<sup>52</sup> This theory takes into account only the first four above mentioned mechanisms (viscous, thermal, intrinsic, and scattering losses).

The viscous losses of the acoustic energy occur due to the shear wave generated by the particle oscillating in the acoustic pressure field. The amplitude of the shear wave decays exponentially with the distance from the particle surface. The dimension characteristic of this decay is the so-called "viscous depth"  $\delta_v$ . It is equal to the

distance from the particle surface at which amplitude drops  $e$  times

$$\delta_v = \sqrt{\frac{2\nu}{\omega}} \quad (5)$$

where  $\nu$  is kinematic viscosity and  $\omega$  is angular frequency.

The reason for the thermal losses is the temperature gradients generated near the particle surface. These external and internal temperature gradients appear due to the thermodynamic coupling between pressure and temperature. The corresponding "thermal depth" determines how far the temperature wave penetrates into liquid

$$\delta_t = \sqrt{\frac{2\tau_0}{\omega\rho_0 C_p^0}} \quad (6)$$

where  $\tau_0$  is a thermal conductivity,  $C_p^0$  is a specific heat at constant pressure of the liquid, and  $\rho_0$  is a liquid density.

Both parameters, "viscous depth" and "thermal depth", are frequency dependent. They decrease when the frequency increases. At some certain frequencies they become comparable with the particle radius  $a$ . Attenuation expressed in dB/(cm MHz) reaches maximum at that frequency range. The frequency corresponding to the maximum attenuation is the so-called "critical frequency".

The ratio of the critical frequencies depends at some extent on the ratio of the viscous and thermal depth. The viscous depth is larger than the thermal one in the aquatic dispersions.<sup>15</sup> As a result, the critical frequency of the thermal losses  $\omega^{th}$  is almost always much lower than the critical frequency of the viscous losses  $\omega^v$ .

Significant difference between the critical frequencies means that one can neglect often the one mechanism of the sound attenuation in favor of the other. For instance, the viscous losses are dominant for the dense rigid solid submicrometer particles within the frequency range from 1 to 100 MHz. The thermal losses are dominant for the emulsions and low density dispersions like latices.<sup>1</sup>

The mechanism of the scattering losses is quite different compared to the viscous and thermal losses. The acoustic scattering mechanism is similar to the light scattering. Acoustic scattering does not produce the dissipation of the acoustic energy. Particles simply redirect the part of the acoustic energy flow and as a result this portion of the sound does not reach the sound transducer.

As mentioned above, acoustic theory for the dilute dispersed system is completed, whereas theory for the concentrated system, especially polydisperse, is far from being done. There are three different approaches to the concentration dependent effects reviewed by Harker and Temple:<sup>53</sup> phenomenological, coupled-phase model, and multiple scattering treatment. The goal of these approaches is to incorporate particle-particle interaction into the acoustic theory.

Dispersed particles oscillating in the acoustic pressure field generate several waves: long scale compression wave and short scale shear and temperature waves. These waves could interfere with other particle motion, which could be effectively described as particle-particle interaction.

The particle-particle interaction through the long scale compression waves is a part of the scattering mechanism of the sound attenuation in the concentrated system. The multiple scattering treatment is the most suitable to describe this effect. There is quite elaborated theory of the multiple scattering reviewed by the Harker and Temple.<sup>53</sup> This aspect of the concentration effects in the acoustic spectroscopy is less important for the colloid

science because scattering losses exhibit itself for large particles and high frequencies.

The particle-particle interaction through the shear and temperature waves is much more important for the colloid science. It affects the thermal and viscous losses mechanisms, which are dominant in the dispersions of the small particles. Particle-particle interaction causes the shift of the acoustic spectra to the higher frequencies. This shift can be very significant. For instance, our dilution experiment with the rutile dispersion<sup>22</sup> shows the shift of the characteristic frequency from 15 MHz for 4 wt % to above 100 MHz for 74.6 wt %. The theory of the sound propagation must take into account this effect. Otherwise the error of the particle size calculation can be enormous.

Fortunately, it turned out that the sensitivity of the viscous losses and thermal losses to the particle-particle interaction is different. Dilution experiments performed in other works<sup>22,23</sup> proved that the viscous loss mechanism is very sensitive to the hydrodynamic particle-particle interaction. At the same time, the contribution of the thermodynamic particle-particle to the thermal losses mechanism is insignificant for the volume fractions up to 30 vol %. This peculiarity explains the success of the acoustic spectroscopy with emulsions and latices.<sup>1</sup>

Nevertheless, there is definite need to modify the viscous losses theory by implementing hydrodynamic particle-particle interaction. There were several attempts to adjust the viscous losses theory for the concentrated system.<sup>1,4,9,21,53</sup> The last one<sup>22</sup> combines together the achievements of the previous works. It explores the "coupled phase approach"<sup>4,53</sup> generalizing it for the polydisperse system. The "cell model" provides an expression for the particle drag following Pendse and Strout.<sup>2,21</sup> At the same time the "cell model" concept has been generalized for the polydisperse system as well.<sup>22</sup>

The new theory of the viscous losses has been successfully tested experimentally with the concentrated rutile dispersion.<sup>22</sup>

Thus, we can conclude that the existing theory of the acoustic attenuation makes it possible to calculate PSD in the concentrated dispersions.

**Advantages and Restrictions of Acoustic Spectroscopy.** (a) **No Calibration.** A major advantage of acoustic spectroscopy is that it does not require a calibration using a colloid with a known PSD. In the preferred mode of the acoustic spectroscopy the acoustic signal is recorded as a function of the gap between the transmitter and receiver. Since the coefficient  $\alpha$  depends only on the rate of change of the acoustic signal with distance, it does not require any absolute calibration of the transducer response. Furthermore since the coupling losses between the transducer and sample are independent of this gap, we also do not need to compute the acoustic impedance of the sample.

(b) **PSD at Zero Density Contrast.** Acoustic spectroscopy is able to characterize particle size distribution when the density of the particles and surrounding media are similar. Dispersed systems like latices and emulsions are very important application of the acoustic spectroscopy. Sound attenuation in these systems is related to the mechanism of the "thermal losses". As a result, attenuation spectra depend on the thermodynamical properties of the dispersed phase and dispersion medium.

(c) **PSD Independent of Charge or Double Layer Model.** The major feature of acoustic spectroscopy is associated with the theoretical interpretation of the experimental data.

It is better to measure the value of the sound attenuation independently rather than calculated from the impedance measured with extremely high accuracy. The attenuation spectra provide important independent information about

particles. This information is independent of the particles' electrosurface properties.<sup>2</sup> Thus, attenuation spectra can be considered as a source of the independent information about particle size distribution.

(d) **PSD for Zero Charge Systems.** The important advantage of the attenuation measurements is the ability to characterize uncharged dispersed systems. Electroacoustic characterization requires particles to be sufficiently charged even for particle size distribution characterization. Decrease in charge leads to the deterioration of the signal-to-noise ratio. Experimental data becomes noisier and calculated parameters are less reliable.

(e) **PSD at High Conductivity.** Acoustic spectroscopy makes it possible to characterize the particle size distribution in the high conducting dispersed systems. Characterization of such systems with the electroacoustic spectroscopy is often impossible because of the parasitic electroacoustic signal.

(f) **Characterization of the PSD of the Conducting Particles.** Acoustic spectroscopy makes it possible to characterize the size distribution of the conducting particles. It is shown further in this paper that the characterization of such systems with the electroacoustic spectroscopy is practically impossible.

(g) **The Existence of the Theory for the Concentrated Systems.** The theory, which is valid in the concentrated system, is necessary to explore the main advantage of acoustic spectroscopy over light scattering. Fortunately, the dilute case theory of the sound attenuation in the emulsions and latices<sup>52</sup> is valid even at the high concentration.<sup>23</sup> The concentrated case theory describing the sound propagation through the dispersions with the high density contrast has been created in ref.<sup>22</sup>

Creation of the electroacoustic theory valid in the concentrated system is a much more complicated task because an additional electrical field is involved.

(h) **Unable To Determine Electroacoustic Properties.** Acoustic spectroscopy provides no way to characterize the electrosurface properties of the particles. Attenuation and sound speed spectra are virtually independent of the electrokinetic losses. As a result they give no information about  $\zeta$  potential. This is the biggest disadvantage of the acoustic spectroscopy.

## Electroacoustic Spectroscopy

**CVP and ESA for Characterizing Electroacoustic Spectroscopy.** Whereas acoustic spectroscopy describes the combined effect of the six separate loss mechanisms, electroacoustic spectroscopy, as it is presently formulated, emphasizes only one of these interaction mechanisms, the electrokinetic losses.

In acoustic spectroscopy sound is utilized as both the excitation and the measured variable, and therefore there is but one basic implementation. In contrast, electroacoustic spectroscopy deals with the interaction of electric and acoustic fields and therefore there are two possible implementations. One can apply a sound field and measure the resultant electric field which is referred to as the colloid vibration potential (CVP), or conversely one can apply an electric field and measure the resultant acoustic field which is referred to as the electronic sonic amplitude (ESA).

First let us consider the measurement of CVP. When the density of the particles  $\rho_p$  differs from that of the medium  $\rho_m$ , the particles move relative to the medium under the influence of an acoustic wave. This motion causes a displacement of the internal and external parts of the double layer (DL).<sup>55,56</sup> This phenomenon is usually

referred to as a polarization of the DL.<sup>56</sup> This displacement of opposite charges gives rise to a dipole moment. The superposition of the electric fields of these induced dipole moments over the collection of particles gives rise to a macroscopical electric field which is referred to as the colloid vibration potential (CVP).<sup>31</sup> Thus, the fourth mechanism of particle interaction with sound leads to the transformation of part of the acoustic energy to the electric energy. This electric energy may then be dissipated if the opportunity for the electric current flow exists.

Now let us consider the measurement of ESA which occurs when an alternating electric field is applied to the disperse system.<sup>32,33</sup> If the zeta potential of the particle is greater than zero, then the oscillating electrophoretic motion of the charged dispersed particles generates a sound wave.

Both electroacoustic parameters CVP and ESA can be experimentally measured. The following expressions give their relationship with the system parameters according to O'Brien<sup>32</sup>

$$ESA = C\varphi\mu_e \frac{\rho_p - \rho_m}{\rho_m} \frac{Z_g Z_s}{Z_g + Z_s} \quad (7)$$

$$CVP = C'\varphi\mu_e \frac{\rho_p - \rho_m}{K^* \rho_m} \frac{Z_g Z_s}{Z_g + Z_s} \quad (8)$$

where  $C$  and  $C'$  are calibration constants independent of the properties of the dispersed system,  $\varphi$  is the volume fraction,  $\mu_e$  is the dynamic electrophoretic mobility,  $K^*$  is the complex conductivity of the dispersed system,  $Z$  is the acoustic impedance, and indexes  $g$  and  $s$  correspond to the sound transducer and dispersed system.

The CVP or ESA spectrum is the experimental output from electroacoustic spectroscopy. Both of these spectra depend on the dynamic electrophoretic mobility, which contains information about  $\zeta$  potential and PSD. The first theory of the dynamic electrophoretic mobility, created by Dukhin,<sup>57</sup> works at the low frequency. That's why O'Brien has created the new theory<sup>54</sup> valid at the frequency range important for the electroacoustic spectroscopy.

Only one of the electroacoustic spectra is required because both of them contain essentially the same information about the dispersed system. Both CVP and ESA are complex parameters. The real and imaginary parts of these parameters contain the same information according to the Kramers–Kronig relationships.<sup>58</sup> Either the real or imaginary component is sufficient in principle to characterize the system. However, it turns out that the measurement of the magnitude and phase of CVP and/or ESA is more effective.<sup>32,33</sup> The phase spectra are more suitable for the particle size distribution (PSD) calculation because it is independent of the  $\zeta$  potential. However, the dependence of the phase on the surface conductivity might still create some problems. The magnitude spectra provide information about the  $\zeta$  potential for known from the phase PSD.

The acoustic impedance  $Z$  relates the acoustic ( $V$ ,  $\alpha$ ) and electroacoustic (CVP, ESA) parameters according to eq 4, eq 7, and eq 8. However, this does not mean that the combination ESA or CVP with the acoustic impedance  $Z$  gives the complete characterization of the disperse system, including attenuation of the sound. Electroacoustic parameters and impedance should be measured

with very high accuracy in order to gain the complete characterization of the disperse system. The contribution of the sound attenuation to the impedance is very small. For instance, attenuation of the 32 wt % rutile in water with the particle diameter 0.33  $\mu\text{m}$  varies from 4 to 8 dB/(cm MHz) in the frequency range between 1 and 100 MHz.<sup>22</sup> The contribution of the attenuation to the acoustic impedance of this concentrated rutile dispersion varies from 1.2% for 1 MHz to 1.9% for 100 MHz according to the eq 4.

The conversion electroacoustic spectra into the PSD requires a theoretical model of the electroacoustic phenomena. This conversion procedure is much more complicated for electroacoustics compared to the simple acoustics. The reason for the additional problems relates to the additional field involved in the characterization, electric field. The theory becomes much more complicated because of this additional field. As a result even the most sophisticated existing theory, created by O'Brien,<sup>54</sup> explores additional assumptions. However, even this dilute case theory has not been completed. It is shown in the next section that existing theory does not account for dispersed systems containing flexible or conducting particles.

Electroacoustic theory available now is valid only for the dilute case. The first attempt made by Rider and O'Brien<sup>59</sup> to generalize this theory for the concentrated case reveals a great deal of the complicated theoretical problems. As a result, the electroacoustic spectroscopy in the current version is applicable for the characterization of only dilute dispersed systems.

**Compression Acoustic Waves in the Electroacoustics.** There are two different approaches to electroacoustic theory. The first was suggested by Enderby<sup>24</sup> and Enderby and Booth.<sup>29</sup> The second was suggested many years later by O'Brien.<sup>54</sup> Both approaches assume liquid being incompressible at the frequencies for which the wavelength exceeds the particle radius  $a$

$$\lambda > a \quad (9)$$

As a result, both approaches consider only shear waves and completely neglect all effects associated with compression waves. This is quite surprising in view of the great importance of compression waves in the general theory of sound attenuation.<sup>51–53</sup> Thermal losses related to these compression waves often predominate over the viscous losses caused by shear waves even at low frequencies. This previous neglect of the compression wave part of the picture encourages us to consider the possible impact of the compression waves in the electroacoustic phenomena, particularly with regard to CVP.

According to attenuation theory, the compressibility of the liquid media and the particle leads to the appearance of a thermal layers at the surface of the particle which can be described by a gradient in the temperature  $T$ . Acoustic energy is transformed to the heat in these layers. Thus, compressible waves appear in the acoustic theory through the temperature gradients.

These same temperature gradients may contribute to the electroacoustic phenomena. However, it turns out that there is a mechanism of straight coupling between compression waves and electric fields around the disperse particle. An approach suggested by Enderby and Booth seems more preferable to explain this mechanism.

Aqueous dispersions of nonconducting rigid solid particles are considered first. The next step is aqueous dispersions of charged conducting particles.

(56) Dukhin, S. S.; Derjaguin, B. V. *Electrokinetic Phenomena. Surf. Colloid Sci.*; Matijevic, E., Ed.; John Wiley & Sons: New York, 1974; Vol. 7.

(57) Vorobyeva, T. A.; Vlodavets, I. N.; Dukhin, S. S. *Colloid. J. USSR* 1970, 32, 189.

(58) Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media*. Pergamon Press: London, 1960.

(59) Rider, P. F.; O'Brien, R. W. The Dynamic Mobility of Particles in a Non-Dilute Suspension. *J. Fluid Mech.* 1993, 257, 607–636.

According to Enderby and Booth, the electric potential  $\psi$  near a spherical particle is a superposition of an equilibrium potential  $\psi_1$  in the undisturbed DL and a nonequilibrium potential  $\psi_2$  generated by the sound wave. The motion of the liquid relative to the particle surface with the velocity  $v$  disturbs the DL. A hydrodynamic field  $v_1$  for uncharged particles gives the first approximation for  $v$ . Originally, a solution given by Sewell<sup>60</sup> is used for  $v_1$  by Enderby and Booth. This part of their work could be modified using the most recent and more general solution given by Allegra and Hawley.<sup>52</sup> This approximate approach has been applied by Enderby and Booth to describe only linear electroacoustic problems. They retain only terms which are linear with the pressure gradient  $\nabla P$ . Nonlinear electrohydrodynamic effects might be also important according to the recent works made by Murts-ovkin and Muller.<sup>61,62</sup>

The calculation of the  $\psi_2$  in the work<sup>24</sup> is very complex. However, this calculation can be dramatically simplified using a modern understanding of the DL dynamics.

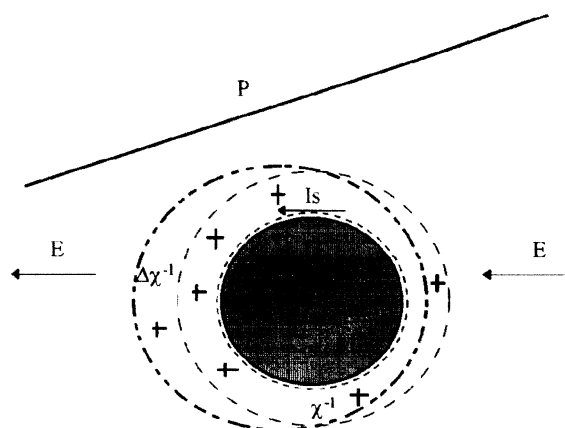
Enderby and Booth formulated electrodynamic equations considering the flow of each specie of ion separately. However, this very detailed consideration is necessary only at low frequencies in the kilohertz range.<sup>55,57,63</sup> This is about 3 orders of magnitude lower than the frequencies usually used for the electroacoustic experiments, which are usually performed in the megahertz range. It is known that there is no need to consider ionic flows at the megahertz frequencies<sup>63</sup> separately. Electrodynamic phenomena at this frequency range depend on the electric current  $I$  equal to the sum of the ionic flows.

The next simplification is already used in O'Brien's theory. It is usually referred to as a "thin double layer" condition.<sup>55,56</sup> The thickness of the double layer  $\chi^{-1}$  is usually much smaller than the particle radius  $a$

$$\chi a \gg 1 \quad (10)$$

The "thin DL" condition allows us to divide the space around the particle into two zones. The first zone near the particle surface is thin and it contains a mobile electric charge. This is the outer part of the double layer. The second zone lies beyond the double layer and is electro-neutral.<sup>55,56</sup>

A liquid motion relative to the particle surface causes the mobile electric charge in the outer part of the DL to move. In other words, a hydrodynamic flow generates electric surface current  $I_s$ . At the same time, there is no current generated by the hydrodynamic flow beyond the DL because that zone is electroneutral. Nevertheless, electric current should pass through this electroneutral zone in order to compensate for the surface current. This is the general law of electric current conservation. The only one way to generate this current requires a long range electric field beyond the DL. This electric field appears due to the particle induced dipole moment  $d_e$ . The superposition of these dipole moments electric fields is CVP. Therefore, the mechanism of the CVP generation could be explained using the notion of the surface current



**Figure 1.** Schematic illustration of the negatively charged spherical particles with the double layer in the pressure field,  $P$ . Dotted line illustrates the outer border of the equilibrium DL, whereas the solid line shows the DL distortion caused by the pressure field.

$I_s$  as a reason for the DL polarization. The picture in the Figure 1 illustrates this explanation.

Electric potential beyond the DL is  $\psi_2$ . Mathematical calculation of the  $\psi_2$  is similar to the calculation of the system dielectric permittivity given by O'Konski.<sup>64</sup> In the case of the dielectric permittivity, the external electric field  $E$  is given whereas surface current  $I_s$  is calculated. In the case of the electroacoustics, the situation is opposite; surface current  $I_s$  is given and external electric field  $E$  is calculated. The simple Laplace equation determines the distribution of  $\psi_2$  beyond the DL:

$$\Delta \Psi_2 = 0 \quad (11)$$

The conditions of the electrical potential and complex induction are the boundary conditions on the particle surface:

$$\psi_2^p(r=a) = \psi_2^m(r=a) \quad (12)$$

$$K^m \frac{\partial \psi_2^m}{\partial \rho} - K^p \frac{\partial \psi_2^p}{\partial \rho} = - \text{div}_s \left( \chi \frac{\partial \psi_2^m}{\partial \theta} + I_s \right) \quad (13)$$

where  $K^* = K + j\omega\epsilon$ ,  $\epsilon$  is dielectric permittivity,  $r$  and  $\theta$  are a spherical coordinate system related to the center of the particle,  $\text{div}_s$  is an operator of the surface divergence, and indexes m and p correspond to the medium and to the particle.

The dipole components of the potentials and surface current can be presented as follows:

$$\psi_2^m = -Er \cos \theta + d_e \frac{\cos \theta}{r^2} \quad (14)$$

$$\psi_2^p = d_e^p r \cos \theta \quad (15)$$

$$I_s = I_s \sin \theta \quad (16)$$

The value of the external field  $E$  generated by the induced dipole moments  $d_e^p$  is equal according to the works in refs

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(62) Murtsovkin, V. A.; Muller, V. M. Steady State Flows Induced by Oscillations of a Drop with an Adsorption Layer. *J. Colloid Interface Sci.* **1992**, 151, 150–156.

(63) Dukhin, S. S.; Shilov, V. N. Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes. John Wiley & Sons: New York, 1974.

(64) O'Konski, C. T. Electric Properties of Macromolecules v. Theory of Ionic Polarization in Polyelectrolytes. *J. Phys. Chem.* **1960**, 64, 605–612.



63 and 65 to the sum of these dipole moments when the system is dilute:

$$E = N_p d_e \quad (17)$$

where  $N_p$  is a number of the particles in the unit of the volume.

Solution of eqs 11–17 with respect to  $E$  gives the following expression

$$E = \frac{I_s \varphi}{2K^m + K^p + \frac{2\chi''}{a}} \quad (18)$$

The simple eq 18 for CVP points out the surface current as a cause of the electroacoustic phenomena. The problem is not completed yet at this intermediate point. The next step is the relationship between surface current  $I_s$  and properties of the shear and compression sound waves.

Shear wave generates surface current because liquid moves relative to the particle surface and involves the ions of the outer DL part. This component of the surface current equals:

$$I_s^{\text{shear}} = \int_a^\infty \rho v_1 dr = \int_a^\infty \epsilon \epsilon_0 \frac{\partial^2 \psi_1}{\partial r^2} v_1 dr \quad (19)$$

where the charge density in the DL  $\rho$  is expressed through the equilibrium potential  $\psi_1$  using the Poisson equation. Hydrodynamic field  $v_1$  comes from the solution of the independent hydrodynamic problem given, for instance, by Allegra and Hawley.<sup>52</sup> There is no need to calculate the integral in eq 19 because it is a priori known that the result of this calculation is the same as that of O'Brien's theory.<sup>54</sup>

$$E^{\text{shear}} = \frac{(\rho_p - \rho_m) \varphi \epsilon \epsilon_0 \zeta}{\rho_m \eta K^*} \quad (20)$$

where the electrophoretic mobility is presented according to Smoluchowski's theory.

Compression wave contributes also to the surface current. This new mechanism of the CVP generation has not been considered before because the all compression effects have been neglected.

Sound wave pressure is different at the opposite ends of the particle (Figure 1). As a result, liquid is compressed differently at these points. At one end it is more compressed than at the other end. The change in the liquid volume leads to the change in the DL thickness. One end of the particle DL is more expanded than the other. The total and local electroneutrality of the DL retains despite these distortions. However, it does not mean that the electric potential distribution in the DL remains the same. Electric potential changes in order to return DL to the equilibrium thickness  $\chi^{-1}$ . The changes in the electric potential are different at the opposite ends of the particle. As a result, the tangential electric field appears. This tangential electrical field generates an additional component of the surface current  $I_s^{\text{comp}}$ . This current equals:

$$I_s^{\text{comp}} = \int_a^\infty \chi''(r) \frac{\partial \psi_1}{\partial \theta} dr \quad (21)$$

where  $\chi''(r)$  is a local conductivity in the double layer.

Surface current  $I_s^{\text{comp}}$  contributes additional term to the CVP which is not reflected in the existed theory. This new mechanism of the electroacoustic phenomena is referred hereinafter to as "compression" in order to distinguish it from O'Brien's "shear" mechanism.

The theory of the "compression" mechanism requires the expression relating  $I_s^{\text{comp}}$  to the pressure gradient and compressibility of the liquid  $\beta^m$  and of the particles  $\beta^p$ . The derivation of such an expression is a mathematically complicated problem beyond the scope of this paper. However, it is possible to make some simple estimations showing the importance of the "compression" mechanism.

First of all, let us consider only high frequency asymptotic when the pressure changes are so fast that the processes in DL cannot reestablish the equilibrium. It means that the frequency is much higher than the Maxwell–Vagner frequency<sup>63</sup> and higher than the characteristic frequency of the surface charge relaxation. This restriction of the frequency allows us to estimate the amplitude of the DL thickness changes  $\Delta\chi^{-1}$  as

$$\Delta\chi^{-1} = \beta(\nabla P) a \chi^{-1} \quad (22)$$

The variation in the DL thickness causes the variation in the surface potential, which could be approximated with  $\zeta$ -potential. Assuming the linear relationship between surface charge and surface potential and, also, keeping in mind that the surface charge is fixed for the high frequency, the amplitude of the  $\zeta$ -potential variation  $\Delta\zeta$  equals:

$$\Delta\zeta = \zeta \frac{\Delta\chi^{-1}}{\chi^{-1}} = \beta \zeta a (\nabla P) \quad (23)$$

The strength of the electric field acting on the DL can be estimated as  $\Delta\zeta/a$ . The approximated value of the surface current, correspondingly, equals:

$$I_s = \frac{\chi''}{a} \frac{\Delta\zeta}{a} = \frac{\beta \zeta \chi''}{a} \nabla P \quad (24)$$

Substitution of this expression for the surface current into eq 18 gives the following approximate expression for the local electric field generated by compression wave in the dispersion of the nonconducting particles:

$$E^{\text{comp}} = \frac{\beta \zeta \chi''}{a K^*} \nabla P \quad (25)$$

The new "compression" mechanism reminds one of diffusiophoresis.<sup>66,67</sup> Diffusiophoretic motion of the particles in the gradient of the electrolyte concentration is also caused by the differences in the DL structure, particularly in the DL pressure, at the opposite particle ends. In the case of the electroacoustics, the gradient of pressure is the given external force of the sound wave. Thus, "compression" contribution to the CVP is proportional to the pressure gradient as well as "shear" contribution.

The ratio of the  $E^{\text{comp}}$  to the  $E^{\text{shear}}$  characterizes the relative importance of the new "compression" mechanism comparing the traditional "shear" one. This ratio equals

$$\frac{E^{\text{comp}}}{E^{\text{shear}}} = \frac{\beta \beta \eta \rho_m \chi''}{\epsilon \epsilon_0 (\rho_p - \rho_m) a} \quad (26)$$

This ratio is always much smaller than 1 for the aquatic

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dispersions with  $\beta = 4 \times 10^{-10} \text{ m}^2/\text{N}$ . It means that the assumption about negligible weak contribution of the compression waves to the electroacoustics is valid for dispersions of rigid solid particles. The compressibility either of the particle or of the liquid should be at least a hundred times bigger in order for the "compression" mechanism to be compared with the "shear" one at long wave range.

The compression mechanism of the CVP generation works for conducting particles also. However, the current through the bulk of the particle replaces the surface current in this case. This bulk current might be much bigger than the surface one because the bulk conductivity  $K^p$  might be much higher than the relative surface conductivity  $\chi^0/a$ . The ratio of the  $E^{\text{comp}}$  to the  $E^{\text{shear}}$  for the conducting particles equals:

$$\frac{E^{\text{comp}}}{E^{\text{shear}}} = \frac{\beta \eta \rho_m K^p}{\epsilon \epsilon_0 (\rho_p - \rho_m)} \quad (27)$$

This ratio is more than 1 when the bulk conductivity is more than 1 S/cm. This condition is definitely valid for the metal particles when they behave like conducting in the liquid medium. The ion exchange resin is another class of dispersion with the high bulk conductivity. Existing theory of the electroacoustic phenomena is not valid for at least these two important classes of dispersions.

It is interesting that the whole idea of the electroacoustic characterization does not work when the "compression" mechanism is important. There is no way to determine particle size from the electroacoustic spectra in this case because the characteristic frequency of the "compression" mechanism is not dependent on the particle size. It is known<sup>63</sup> that the Maxwell–Vagner frequency depends only on the ionic strength.

**Advantages and Restrictions in the Electroacoustic Technique.** (a) **Ability to Characterize Both PSD and  $\zeta$  Potential.** At first blush, electroacoustic spectroscopy seems to offer both particle size and charge measurements with a single measurement technique. How realistic is this? Consider the various assumptions which are necessary for the interpretation of electroacoustic data.

(b) **Calibration with a Known Colloid Required.** Such calibration is the essential part of the electroacoustic spectroscopy. It is a possible source of errors.

(c) **Absence of the Electroacoustic Theory Valid for the Concentrated System.** The electroacoustic theory is the essential part of the electroacoustic spectroscopy. It is necessary for conversion of electroacoustic spectra to PSD and  $\zeta$ -potential. Absence of the electroacoustic theory for the concentrated system makes it hard to explore the main advantage of the acoustic type spectroscopy over light scattering: the ability to characterize a concentrated dispersed system.

(d) **Constant  $\zeta$  Potential Restriction.** O'Brien's theory assumes that all particles have the same  $\zeta$  potential. This assumption might be valid for single component systems if the thickness of the DL  $\chi^{-1}$  is much less than the particles radius  $a$ . This further assumption might indeed be correct for many aqueous disperse systems but it still introduces uncertainty in the measurement, even more so in the case of very small particles or nonaqueous media. More important perhaps is the fact that this assumption makes it impossible to handle the case of mixed component systems, as for example ceramic slurries.

(e) **Double Layer Model Required.** Current electroacoustic theory requires certain simplifying assumptions concerning the nature of the double layer. The

Gouy–Chapmann DL model is the simplest and the most widely used. It is usually applied assuming that the surface conductivity can be ignored. This is the so-called "Smoluchowski" approach. This approach is valid when parameter  $\text{Rel}^{56,63}$  (called  $\lambda$  in O'Brien's works<sup>32,33,54,59,68,69</sup>) is much less than 1.  $\text{Rel}$  equals the ratio of the surface conductivity to the conductivity of the medium  $K$ :  $\text{Rel} = \chi^0/Ka$ . There is considerable evidence, however, that this Smoluchowski approximation is often invalid [56,57, 60–65], especially for particles covered with a surfactant layer which causes additional so-called "anomalous" surface conductivity.<sup>55,56,70–75</sup>

The uncertainties with the DL model affect not only calculated value of the  $\zeta$ -potential but PSD as well.

(f) **Zero Thermal Loss Restriction.** O'Brien's electroacoustic theory<sup>54</sup> neglects the contribution of the compression waves to electroacoustic effects. It is well-known from acoustic theory that both compression and shear waves are generated by dispersed particles in a sound field.<sup>52</sup> O'Brien's electroacoustic theory<sup>32,54,59</sup> does take into account the shear waves, yet totally ignores the compression waves which are necessary to describe the thermal loss mechanism of attenuation.<sup>1,51–53</sup> It has been shown above that although the effect of compression waves can be neglected in electroacoustic phenomena for aqueous dispersions of nonconducting rigid particles, they are in fact the dominant factor for aqueous dispersions of conducting particles and potentially important for nonrigid compressible particles and nonaqueous media.

## A Combined Acoustic and Electroacoustic Spectroscopy

It has been shown that the both acoustic and electroacoustic techniques have significant disadvantages. There is one way to eliminate these disadvantages. Such an optimum acoustic based technique should combine both acoustic and electroacoustic spectroscopy together. The problems of the complicated hardware are less important for the user now because of the possibility of full computerization and automation.

Acoustic spectroscopy based on the attenuation measurement does not require any assumptions about electrosurface properties for particle size distribution calculation. As a result the PSD obtained with the acoustic spectroscopy is more reliable than PSD extracted from the electroacoustic spectra. It means, that acoustic spectroscopy is more preferable for the characterization of the particle size distribution.

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The more reliable PSD coming from acoustic spectroscopy can then be used in the interpretation of the electroacoustic spectra. As a result, the improvement in the PSD reliability leads to the more reliable  $\zeta$ -potential data.

Acoustic and electroacoustic spectra contain information not only about PSD and  $\zeta$ -potential but also about structure, stability, electrostatic parameters like surface conductivity  $\chi''$ , etc. The theory of the acoustic and electroacoustic phenomena allows us to extract this information in principle. Such more complete characterization procedure requires as much experimental data as is possible to collect. The suggested combined technique is more favorable from this viewpoint compared to either only acoustic or only electroacoustic spectroscopy.

Both acoustic and electroacoustic theories use a set of the assumptions and replace a real disperse system with a realistic model system. As a result, the theoretical output data is only an approximation to the real values of the dispersed system characteristics. The degree of this approximation determines the reliability of the particular version of the spectroscopy. It is obvious that reliability increases when more experimental information is involved into the theoretical interpretation. The more experimental information involved, the less assumptions and a more realistic model system could be used in the theoretical analysis. However, measurement of the each new spectrum requires additional sophisticated hardware and the spectrometer becomes more and more complex in operation. Therefore, there is a trade-off between the complexity of the spectrometer and reliability of the output data. This trade-off determines the strategy of the characterization procedure. We believe that the modern level of the electronics and software is sufficient to build spectrometer combining acoustic and electroacoustic spectroscopes together.

## Conclusions

Analysis of the literature shows gradual improvement and development in the acoustic and electroacoustic spectroscopy.

Acoustic and electroacoustic spectroscopy are independent because each of them provides information about independent sets of parameters. Sound attenuation measured with acoustic spectrometer contributes almost nothing to the electroacoustic phenomena. At the same time, the impact of the electroacoustical effects to the sound attenuation is negligibly weak.

The combination of the acoustic and electroacoustic spectroscopy provides a much more reliable and complete characterization of the disperse system than either one of those spectroscopies separately. The reliability of the characterization depends not only on the accuracy of the measurement but also on the reliability of the theoretical model. An existing version of the electroacoustic theory contains more uncertainties than a better established and verified acoustic one. It is shown, for instance, that compression waves neglected in the existing version of the electroacoustic theory are dominant for the conducting particles.

Electroacoustic phenomena are more complicated to be interpreted when comparing the acoustic ones because an additional field (electric) is involved. This problem becomes even more pronounced for a concentrated system. Increase of the volume fraction leads to the higher probability for the system to be structured. The problem of structure is much simpler to be addressed with acoustic spectroscopy because an acoustic spectrometer can be considered at the same time as a micro rheometer.

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