Characterization of Concentrated Dispersions with Several Dispersed Phases by Means of Acoustic Spectroscopy

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Acoustic attenuation spectroscopy can characterize the particle size distribution (PSD) of mixed concentrated dispersions, i.e., systems having more than one dispersed phase. In this paper, we will suggest two models that can be particularly helpful for describing such mixed dispersions. The first "multiphase" model assumes that we can represent the PSD of a real-world dispersion as a sum of separate log-normal distributions, one for each component in the mixed system. For this paper we assume that there are but two components, which reduces the overall PSD to a simple bimodal distribution. The second "effective medium" model further assumes that one needs to determine the PSD of just one component in an otherwise complex mixed system. All other disperse phases are lumped together into an effective homogeneous medium characterized by a composite density, viscosity and acoustic properties. By adopting this viewpoint, we significantly reduce a complex real-world mixture to a simpler dispersion of a single pre-selected dispersed phase in a newly defined "effective medium". We need not even define the exact nature and composition of this new medium since we can simply measure, or perhaps calculate, the required composite density, viscosity, attenuation, and sound speed. The "multiphase" model is most suitable for samples where it is desired to measure the PSD for more than one well-characterized disperse phase. In contrast, the effective medium model is particularly useful where it is desired to measure only one component in a complex poorly defined multicomponent mixture. Experimental results are presented for five different mixtures including alumina, zirconia, silica, and calcium carbonate materials. These tests demonstrate that the mathematical complexity of the "multiphase" model often leads to the familiar "multiple solution problem" whereas the "effective medium" approach is more reliable and robust. Furthermore, the "verification" approach reveals an aggregation phenomena in the PCC−silica mixed dispersion.

Introduction

There are many important natural and man-made dispersed systems containing a high concentration of more than one dispersed phase. For instance, whole blood contains many different types of cells, paint usually consists of latex with added pigment to provide color, and sunscreen preparations include both an emulsion as well as sun-absorbing particles. In many such systems there is a practical need to determine the particle size distribution (PSD) of one or more ingredients. In general, light-based techniques are not well suited to provide this information because most optical methods require the sample to be diluted prior to measurement, thereby distorting or destroying altogether the particle size information being sought. Furthermore, most light-based systems cannot handle multiple disperse phases, even in the most dilute case.

In contrast, acoustic attenuation spectroscopy[1−3] opens an opportunity to eliminate this undesirable dilution step. It is now well-known that acoustic spectroscopy can characterize particles size at concentrations up to 45 vol %.[3−5] Furthermore, acoustic attenuation spectroscopy can

characterize the particle size distribution of concentrated dispersions having more than one dispersed phase These two unique feature makes acoustic spectroscopy very attractive for characterizing the particle size distribution of real-world dispersions.

There are at least three quite different philosophical approaches for interpreting these acoustic spectra.

In the simplest *"empirical"* approach, we forego any size analysis per se and simply observe the measured acoustic attenuation spectra to learn whether, for example, the sample changes with time or if "good" or "bad" samples differ in some significant respect. Importantly, this empirical approach provides useful engineering solutions even in cases where we know nothing about the physical properties of the sample or whether indeed the sample is adequately described by our theoretical model.

In a more subtle *"validation"* approach we assume in advance that we know the correct particle size distribution and furthermore assume the real dispersion conforms to some model. We then use some predictive theory based on this model, as well as the assumed size distribution, to test whether this predicted attenuation matches that actually measured. If the validation fails, it is a very strong indication that the model is inadequate to describe the system at hand.

As an example of this validation approach, consider the case where we construct a mixed system by simply blending two single-component slurries. The PSD of each single-component slurry can be measured prior to blending the mixed system. Since we have control of the blending operation, we know precisely how much of each component is added. If we claim that the combined PSD is simply a weighted average of the individual PSD for each component, we are in effect assuming that there is no interaction

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(2) Dukhin, A. S.; Goetz, P. J. Acoustic and Electroacoustic Spectroscopy. *Langmuir* **1996**, *12* (19), 4334−4344.

(3) Dukhin, A. S.; Goetz, P. J. Acoustic and Electroacoustic Spectroscopy. In *Ultrasonic and Dielectric Characterization Techniques*; Hackley, V., Texter, J., Eds.; American Ceramic Society: Westerville, OH, 1998; pp 77−97.

(4) Dukhin, A. S.; Shilov, V. N; Ohshima, H.; Goetz, P. J. Electroacoustics Phenomena in Concentrated Dispersions. New Theory and CVI Experiment. *Langmuir*, in press.

(5) Dukhin, A. S.; Goetz, P. J. Acoustic Spectroscopy for Concentrated Polydisperse Colloids with High Density Contrast. *Langmuir* **1996**, *12* (21), 4987−4997.

between these components. In this case the prediction theory allows us to compute the theoretical attenuation for this mixed system. If the experimental attenuation spectrum matches the predicted spectrum then the assumption that the particles did not interact is confirmed. However, if the match is poor, it is then likely that the mixing of the two components caused some changes in the aggregative behavior of the system. Perhaps new composite particles were formed by some interaction of the two species. Or perhaps some chemical component in one sample interacted with the surface of another. Many interaction possibilities exist. Nevertheless, it seems appropriate to conclude that a necessary condition to rule out aggregation on mixing is that the experimental and predicted attenuation curves match. In addition we can probably also conclude that an error between theory and experiment is sufficient to say that some form of aggregation or disaggregation on mixing has occurred. We will show that such prediction arguments are indeed able to monitor such aggregation phenomena.

Finally, we can take the ultimate leap and use an *"analysis"* algorithm to search for that particle size distribution which in accordance with the model and the predictive theory best matches the experimental data.

Importantly, both the "validation" and "analysis" approach assume that we can accurately model the real world, while at the same time making some simplifying assumptions. For example, it is common to assume that the particles can be treated as spheres, even though we know that this may not be exactly the case. In this paper, we will suggest two models that can be particularly helpful for describing mixed dispersions.

So it is clear that an acoustic spectrometer, or for that matter any light scattering instrument, does not directly measure particle size. In fact, any technique based on some macroscopic measurement follows more-or-less a four-step procedure. First we measure an acoustic attenuation spectrum (or some optical property in the cases of light-based instruments). Second, we make certain assumptions in translating the real-world sample into a model colloid system more amenable to theoretical treatment. Third, we adopt some predictive theory, which allows us to compute the acoustic attenuation in terms of these model parameters (Mie or Fraunhofer theories in the cases of light scattering). Finally, we construct an analysis algorithm that can find a PSD, which according to the prediction theory and our model colloid yields a theoretical attenuation spectrum that best matches the experimental data.

The prediction and analysis components appropriate to acoustic spectroscopy are not topics for this paper as they are well described elsewhere.[10] Rather, in this paper we want to describe two quite different ways of interpreting the real-world mixed systems in terms of a model colloid.

Whereas there are several papers[6-9] which demonstrate that acoustic spectroscopy is able to characterize bimodal distributions in dispersions where both modes are chemically identical, it is less well-known that acoustics is also suitable for characterizing mixed dispersions where each mode is chemically quite different. The goal of this paper is to explore the capability of acoustic spectroscopy to characterize mixed systems of dissimilar materials.

In this paper, we will suggest two models that can be particularly helpful for describing such mixed dispersions.

The first "multiphase" model assumes that we can represent the PSD of a real-world dispersion as a sum of separate log-normal distributions, one for each component in the mixed system. For this paper we assume that there are only two components, which reduces the overall PSD to a simple bimodal distribution. When we calculate the attenuation of such a multiphase system we take into account the individual density and other particles properties for each component in the mixture. For a bimodal case, the multiphase approach would typically require the analysis algorithm to fit five adjustable parameters: the median size and standard deviation of both modes and the relative mass fraction of each mode. In this work we will assume that the weight fraction of each mode is known in advance. Furthermore, in an effort to avoid the well-known problem of multiple solutions, we will further assume that both modes have the same standard deviation. Altogether, these simplifications reduce the number of adjustable parameters to just three: the median size of each mode and the standard deviation. The implications of these simplifications will be discussed later.

The second "effective medium" model further assumes that one needs to determine the PSD of just one component in an otherwise complex mixed system. All other disperse phases are lumped together into an effective homogeneous medium characterized by some composite density, viscosity, and acoustic parameters. By adopting this viewpoint, we significantly reduce a complex real-world mixture to a simpler dispersion of a single preselected dispersed phase in a newly defined "effective medium". We need not even define the exact nature and composition of this new medium since we can simply measure, or perhaps calculate, the required composite density, viscosity, attenuation, and sound speed. If we assume that the key disperse phase can be described by a log-normal distribution, then we have reduced the degree of freedom to just two adjustable parameters, a median size and standard deviation.

In this paper we evaluate the effectiveness of both the multiphase and the effective medium model using the same set of experimental data. As a result, we gain a better understanding of the restrictions and benefits of each method.

Experimental Section

Technique. The tests described here were performed using a DT-1200 acoustic spectrometer developed by Dispersion Technology, Inc.[11] This instrument has two independent sensors: one for measuring the acoustic attenuation spectra from which it computes the particle size distribution and a second sensor for measuring the electroacoustic signal from it computes ς potential.

Both sensors use pulsed ultrasonic techniques. The acoustic sensor measures the attenuation spectra by means of two piezoelectric transducers. The gap between the transmitter and receiver is variable in software-controlled steps. In default, it

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(8) Dukhin, A. S.; Goetz, P. J. Characterization of Chemical Polishing Materials (Monomodal and Bimodal) by Means of Acoustic Spectroscopy. *Colloids Surf.*, in press.

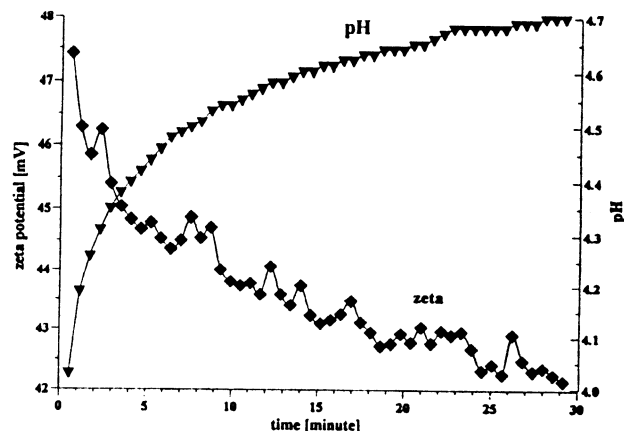(9) Wines, T. H.; Dukhin, A. S.; Somasundaran, P. Acoustic spec-

Figure 1. Equilibration of 3 vol % zirconia slurry prepared in 10^{-2} M KCl with pH adjusted initially to 4. It is seen that equilibration takes about 2 h.

Figure 2. Titration of the PCC slurry with 0.1 g/g of hexametaphosphate solution.

default, it changes from 3 to 100 MHz in 18 logarithmic steps. The number of pulses collected for each gap and each frequency is software controlled in order to reach a target signal-to-noise ratio for each point on the selected gap/frequency grid.

The acoustic sensor also measures the group sound speed at a chosen frequency using the change in transit time of the pulse across the variable gap. The instrument automatically adjusts the time sampling of the received pulse depending on the value of the sound speed, which is necessary to eliminate artifacts such as excess attenuation at low frequencies.

A single attenuation spectrum is measured using default conditions in about 5 min. The user can speed up measurement by changing setup parameters, and successive measurements on the same sample are always faster as the software automatically discards unproductive points on the gap/frequency grid.

An analysis program calculates the particle size distribution from the attenuation spectra. It uses an error analysis in order to determine whether a log-normal, bimodal or modified log-normal[12] particle size distribution best fits the experimental data. The goal of the analysis program is to find that PSD which minimizes the difference between the attenuation spectra predicted by theory and that measured experimentally.

The precision and accuracy of the acoustic spectrometer has been tested with several different model systems.[10] The precision and accuracy of the particle size measurement is about 1%.

The total required sample volume is about 100 mL. A magnetic stirrer prevents sedimentation and provides mixing of reagents during titration. The instrument also measures conductivity, pH, and temperature and provides digitally controlled burets for dispensing chemical reage4nts during automated titration protocols.

Materials. We used three pigments from Sumitomo Corp.: AKP-30 alumina (nominal size 0.3 μm); AA-2 alumina (2 μm); TZ-3YS zirconia (0.3 μm). In addition we used precipitated calcium carbonate (PCC) supplied by Specialty Minerals Corp. (0.7 μm) and Geltech silica (1 μm).

Slurries of the AA-2 alumina and the zirconia were prepared in such a manner as to have quite good aggregative stability. Each slurry was prepared at 3 vol % by adding the powder to a 10^{-2} mol/L KCl solution, adjusted initially to pH 4 in order to provide a significant ζ potential. Although the alumina showed very quick equilibration, the zirconia required about 2 h for the ζ potential and pH to equilibrate as shown in Figure 1. Both slurries were judged to be quite stable under these conditions as indicated by the absence of any noticeable settling.

Preparation of a 3 vol % PCC slurry was more problematic since the ζ potential right after dispergating was very low (1.3 mV). Control of pH alone was insufficient, and we therefore used sodium hexametaphosphate in order to increase the surface charge and improve the aggregative stability of this slurry. To
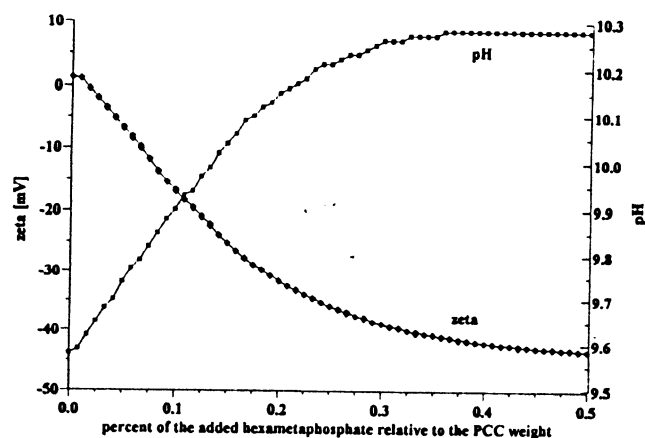
determine the optimum dose we ran a ζ-potential titration, the results of which are shown in Figure 2. The ζ potential reaches saturation at a hexametaphosphate concentration of about 0.5 wt % relative to the weight of the PCC solid phase.

The Geltech silica and the AKP-30 alumina were used only as dry powders, being added to the PCC slurry as needed.

Experimental Protocol. The goals of the experiment were met in the following steps: (1) Three single component slurries of alumina AA-2, zirconia, and PCC, respectively, were prepared as described above. (2) The attenuation spectra of these single component slurries were measured, and the particle size distribution for each was calculated. (3) Three mixed alumina/zirconia slurries were prepared by blending the above slurries in different proportions, and the attenuation spectra for each mixture were measured. (4) Geltech silica powder was added to the initial PCC slurry, and the attenuation spectra were measured for this mixed system. (5) AKP-30 alumina powder was added to the initial PCC slurry, and the attenuation spectra for this mixed system were measured. (6) The particle size distribution was calculated for all of the mixed systems using the "multiphases model". (7) The properties of the "effective medium" were calculated for all mixtures. (8) The particle size distribution for each of these mixed systems was calculated using the "effective medium model". (9) The results of the particle size calculation using two different approaches were compared. (10) The validation approach was used to test for possible particle interactions in the mixed systems.

Results and Discussion

The experimental attenuation spectra for the three single component slurries and five mixtures are shown in Figures 3 and 4. To demonstrate reproducibility, each sample shown in Figure 3 was measured at least three times. Mixture 1, in fact, was measured yet a fourth time after a fresh sample was loaded just to show that sample handling was not a factor. It is clear that the reproducibility is sufficient for resolving the relatively large differences in attenuation between different samples.

The attenuation spectrum for the single component slurries of the AA-2 alumina, the zirconia, and the PCC allows us to calculate the particle size distribution for each of these materials. The calculated sizes are given in Tables 1 and 2, and it is seen that these acoustically defined sizes agree quite well with the nominal sizes given by the producers of these materials.

As shown in Figures 3 and 4, the attenuation spectra of the mixtures differ significantly from the attenuation spectra of the single-component slurries. This difference in the attenuation spectra reflects the differences in both the particle size distributions and the density of the constituent components in the mixtures

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Table 1. Characteristics of Alumina AA-2 and Zirconia TZ-3YS Slurries and Their Mixtures

	initial		mixture 1		mixture 2		mixture 3	
	alumina	zirconia	alumina	zirconia	alumina	zirconia	alumina	zirconia
vol fraction, %	3	3	1.55	1.45	1.85	1.15	2.28	0.72
weight fraction, %	10.96	15.91	5.5	7.9	6.6	6.3	8.2	4
eff viscosity, cp			0.92		0.93		0.94	
eff density, g/cm3			1.04		1.05		1.06	
att(M_0)	1.593		1.21		0.982		0.823	
att($M1$)	0.0845		0.0642		0.0521		0.0437	
att($M2$)	−1.251		−0.95		−0.771		−0.646	
att($M3$)	0.528		0.401		0.326		0.273	
Parameters of the Particle Size Distributions, Effective Medium Approach								
median log-normal, μm	2.15 ± 0.02	0.33 ± 0.006		0.293 ± 0.006		0.303 ± 0.005		0.317 ± 0.003
std dev	0.26	0.43		0.38		0.378		0.372
fitting error, %	6.6	1.9		1.4		1.2		0.95
Parameters of the Particle Size Distributions, Two Dispersed Phases Approach								
median size, μm			0.565 ± 0.002	0.558 ± 0.001	2.922 ± 0.088	0.352 ± 0.005	3.582 ± 0.182	0.303 ± 0.003
std dev				0.53		0.3		0.21
fitting error, %				5		7.6		4.4

Table 2. Characteristics of PCC Slurry and Its Mixtures with Alumina AKP-30 and Silica Geltech

	initial PCC	nitial silica	PCC and silica		PCC and alumina	
		powder	PCC	silica	PCC	alumina
vol fraction, %	10.55		9.19	6.29	10.27	2.52
weight fraction, %	23.53		19.6	11.3	21.6	8.1
eff viscosity, cp	1.125		1.094		1.118	
eff density, g/cm³	1.17		1.13		1.15	
att(M_0)	1.053					
att(M_1)	4.431					
att(M_2)	3.648					
att(M_3)	0.9296					
Parameters of the Particle Size Distributions, Effective Medium Approach						
median log-normal, μm	0.684	1.26		0.454		0.325
std dev	0.31	0.35		0.015		0.015
fitting error, %	1.1	1.3		7.5		2.4
Parameters of the Particle Size Distributions, Two Dispersed Phases Approach						
median size, μm			0.449	0.681	0.798	0.2715
std dev				0.16		0.19
fitting error, %				8		1.9
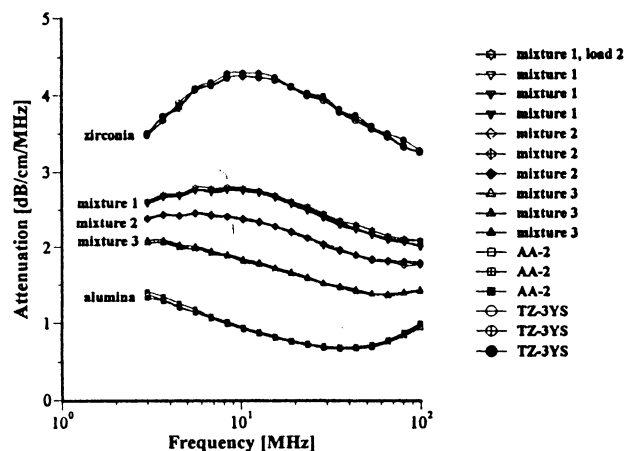
Figure 3. Experimental attenuation spectra for initial alumina AA-2 and zirconia TZ-3YS from Sumitomo and their mixtures with weight fractions given in the Table 1. This figure illustrates reproducibility, including two loads for mixture 1.
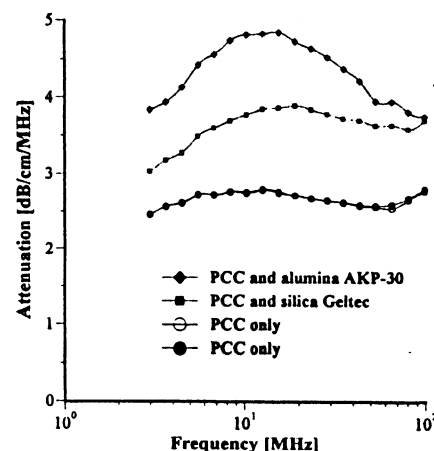
Figure 4. Experimental attenuation spectra for initial PCC slurry and its mixture with the added silica and alumina powders. Weight fractions are given in the Table 2.

We want to compare the effectiveness of the "multiphase" and the "effective medium" approach in calculating the PSD of these five different mixed systems.

First let us consider the more or less straightforward "multiphase" model. To use this approach we need only

that each mode corresponds to one disperse phase material. For instance in the alumina/zirconia mixture the smaller mode corresponds to the zirconia and the larger mode corresponds to the alumina. The software takes into account the difference in densities between materials of the first and the second modes. The PSD of each mode is
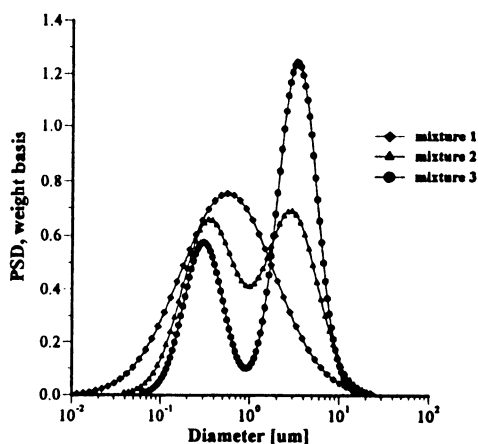
Figure 5. Particle size distributions calculated for alumina–zirconia mixtures using the "multiphases model". The smaller size mode corresponds to zirconia; the larger size mode is alumina AA-2. Weight fraction and PSD parameters are given in the Table 1.
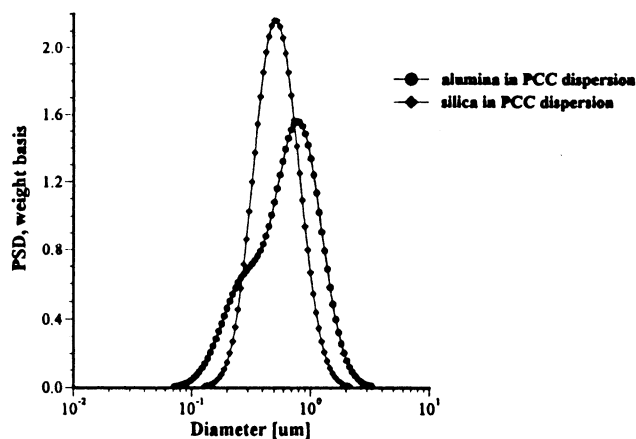

Figure 6. Particle size distributions calculated for PCC–alumina and PCC–silica mixtures using the "multiphases model". Weight fraction and PSD parameters are given in the Table 2.

implementation assumes that both modes have the same standard deviation. The software searches for some combination of three adjustable parameter (two median sizes and their common standard deviation) that provide the best fit to the experimental attenuation spectra. It assumes the relative content of the modes to be known.

The corresponding PSD for these five mixed systems are shown in Figures 5 and 6. The parameters of these PSD are given in Tables 1 and 2. It is seen that in some cases this "multiphase" approach yields approximately the correct size. For instance, the two zirconia/alumina mixtures with a lower zirconia content (mixtures 2 and 3) have almost the correct size combination. The size of the alumina particles is somewhat higher than expected (2.15 μm) but is still rather acceptable. We can say the same about the PCC/alumina mixture from Table 2. The difference of the sizes relative to the nominal values does not exceed 10%.

However, the multiphase model appears a complete failure for the alumina/zirconia mixture 1 as well as the PCC/silica mixture. It is not clear yet why this "multiphases model" works for some systems and not for others. We think it probably is related to the fact that the present software assumes that both particle size modes have the same width. It is seen that the single component zirconia slurry has a PSD that is much broader (std dev = 0.43)

than the PSD of the AA-2 alumina (std dev = 0.26). The bimodal searching routine finds the correct intermediate value for the standard deviation (0.3) only for mixture 2. It is interesting that this PSD solution is the closest match to the superposition of the initial PSD. The standard deviations for the other two mixtures are out of range completely, and the corresponding PSD also deviate from the expected superposition.

This observation allows us to conclude that our restriction that the standard deviation be the same for both modes might itself create an artificially wrong solution. It is easy to eliminate this restriction, but as one adds additional degrees of freedom, it is not uncommon to be faced with the problem of multiple solutions.

This multiple solution problem appears when the error function (difference between experimental and theoretical attenuations) has several local minimums with different combinations of the adjustable parameters. In general, the problem of multiple solutions increases as the number of adjustable parameters increases. It seems clear that the maximum number of adjustable parameters to avoid multiple solutions is not a fixed number but rather depends on a combination of factors: the accuracy and amount of experimental data points; the degree to which the real-world sample is described by the model; how accurately the key parameters of the colloid such as weight fraction, density, etc., are known. Our experience is that bimodal PSD with even four adjustable parameters sometimes exhibit multiple solutions. We have found ways to resolve these multiple solutions in the case of single-component dispersions; however, the situation is more complicated for mixed dispersions with two or more chemically different components. For this reason, we restricted the number of the adjustable parameters to only 3 for this work.

These results indicate that the "multiphase" model might sometimes lead to wrong solutions and it is unclear at this point how to completely eliminate the problem.

In contrast, the "effective medium" approach circumvents this problem by addressing only the question of determining a simple log-normal distribution that describes only one disperse phase in an otherwise complex mixture. Since we are then dealing only with two adjustable parameters (median size and standard deviation), the possibility for multiple solutions is most likely diminished. On the downside, when using the "effective medium" approach, we need to perform an additional experiment to measure the properties of this "effective medium" and this may not always be possible or without other difficulties.

In the case of the PCC mixtures with the added alumina or silica, the original PCC slurry itself serves as the "effective medium". We need just three parameters to characterize this "effective medium", namely, density, viscosity, and attenuation. Importantly, all three parameters can be directly measured if we have access to this medium. The attenuation is the most important of these three required parameters. It is also the most challenging to characterize because we need the attenuation of this medium as a function of frequency from 3 to 100 MHz. The current version of the DT 1200 software allows us to define the attenuation of the effective medium the same way we would normally define the "intrinsic attenuation" of even a pure liquid medium. This intrinsic attenuation as measured in dB/(cm/MHz) can be described in terms of a polynomial function:

$$\text{att}(f) = \text{att}(M_0) + f \, \text{att}(M_1) + f^2 \, \text{att}(M_2) + f^3 \, \text{att}(M_3)$$
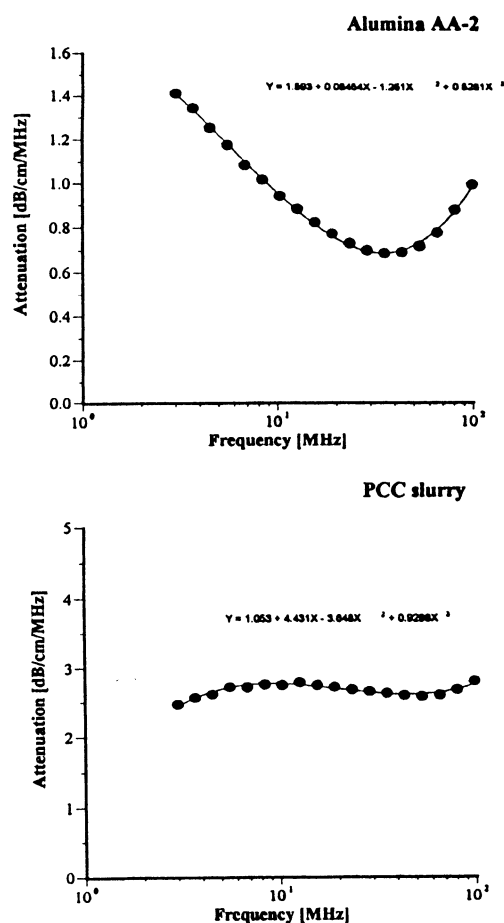
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Alumina AA-2

PCC slurry

Figure 7. Experimental attenuation spectra measured for individual alumina AA-2 slurry and PCC slurry with polynomial fit.

Zirconia

Figure 8. Particle size distribution calculated using the "effective medium model". In the case of zirconia the alumina AA-2 dispersion is the effective medium. Attenuation of the alumina is reduced according to volume fractions from Table 1. Density and viscosity are adjusted as the effective medium. In the case of alumina AKP-30 and silica the PCC dispersion is the effective medium.

Alumina and silica in PCC slurry

Figure 9. Experimental and theoretical attenuation for zirconia—alumina mixture 1 and PCC—silica mixture. Theoretical attenuations are calculated for the best analysis result and for combined PSD build from the individual distributions assuming no particle aggregation.

where f is frequency in MHz and M_0, M_1, M_2, and M_3 are the polynomial coefficients.

For example, in the simplest case we can say that our effective medium is just water. Water has an attenuation that for practical purposes can be said to simply increase as a linear function of frequency if attenuation is expressed in dB/(cm/MHz). Thus M_0, M_2, and M_3 are zero and M_2 represents this linear dependence.

To use the effective medium approach for mixed systems, we simply need to define new coefficients to describe the intrinsic attenuation of this new medium. In the case of the alumina/zirconia mixtures we use the alumina slurry as the "effective medium". The coefficients for the alumina slurry can be calculated by doing a polynomial fit to the attenuation data as shown in Figure 7A. These coefficients are also given in Table 1. Similarly, the coefficients for the PCC "effective medium" can be calculated from a polynomial fit of the attenuation data for that material as shown in Figure 7B. Likewise, these coefficients are given in Table 2.

We should keep in mind that the initial alumina slurry is diluted when we mix it with increasing amounts of the zirconia slurry. As a result, we need to recalculate the attenuation coefficients for each mixture taking into account the reduced volume fraction of the alumina in each mixture. The suitably modified values for the attenuation coefficients of the effective medium for all three alumina/zirconia slurries are also given in the Table
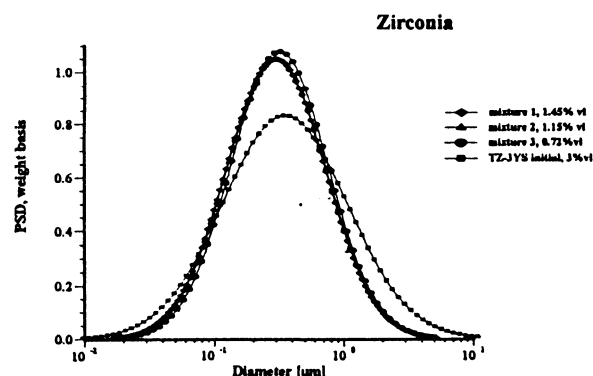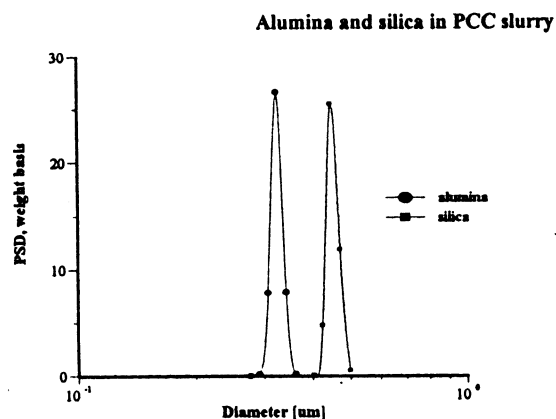
medium, and therefore, the coefficients for the PCC effective medium are the same for both mixtures.

For an aqueous medium, the software automatically calculates the intrinsic attenuation of water and subtracts this from the measured attenuation to deduce the attenuation caused solely by the presence of the disperse particles. When using the "effective medium" model, the software actually works in the same way, except that the intrinsic attenuation of water is replaced by the attenuation of this new effective medium. For instance, in the case of the PCC/alumina mixture the software calculates the attenuation due to the PCC contribution and subtracts it from the total attenuation of the mixture. The residual part corresponds to the attenuation due to the alumina particles and is the source of the particle size information for the alumina component. The software assumes a log-normal PSD and fits this residual attenuation using the median size and standard deviation as adjustable parameters.

This effective medium approach allows us to calculate the particle size distribution of the zirconia in the alumina/zirconia mixtures and of the silica or the alumina in the case of PCC mixtures. The corresponding values are shown in Tables 1 and 2. Figures 8 and 9 illustrate the

slurry. The fitting error is much smaller than in the "multiphase model" which is an additional indication of the consistency.

In the case of PCC mixtures the situation is more complicated. We have a very good correlation with the nominal size for the AKP-30 alumina for PCC—alumina mixture with a good fitting error.

The other PCC based mixture gives a particle size which is twice smaller than expected. You can see from the Table 2 that the calculated size of the silica Geltech is only 0.454 μm whereas the nominal size is at least 1 μm. We measured acoustically for this silica even larger size of 1.26 μm. It might happen because of the dispersing problems. We have found that this silica is difficult to disperse properly even at high pH and high ζ potential. For instance, we measure ζ potential of -66 mV for this silica at pH 11 but even this was apparently not sufficient to disperse it completely.

Summarizing the analysis results for these five mixtures, we conclude that in the case of the three mixed dispersions (alumina—zirconia mixtures 2 and 3 and the PCC—alumina mixture), the "multiphase model" and the "effective medium model" gave similar results and reasonable PSD. For the other two mixtures, the results are more confusing. We suspect that the failure of the "multiphases model" for the alumina—zirconia mixture 1 is related to the restriction on the PSD width, but particles aggregation is still a candidate as well. In the case of the PCC—silica mixture a double failure of both modes certainly points toward particle aggregation.

We can evaluate these ideas about aggregation of the two troubled mixtures using the "validation" approach. To do this we must first compute the total PSD using the known PSD of the individual single component dispersions. Next, we calculate the predicted attenuation for this combined PSD. This predicted attenuation should agree with the experimental spectrum for the mixed system if there is no particle interaction between the species.

Figure 10 illustrates the predicted and experimental attenuation spectrum for the zirconia—alumina mixture 1 and the PCC—silica Geltech mixture. For both mixtures we have also added the predicted attenuation corresponding to the best PSD calculated using the "multiphase model" analysis.

It is seen that in the case of the zirconia—alumina mixture a superposition PSD generates an attenuation spectrum that fits experimental spectra much better than the best "multiphase model" analysis PSD. The fitting error has improved from 5% to 2.3% and becomes comparable with the best fitting errors of the "effective medium" model. This correlation between prediction and experiment proves that our concern about using a common standard deviation for both modes was well founded. The prediction program allows us to apply independent standard deviation for each mode of the PSD, and as a result, we achieve much better fitting than in the case of the analysis "multiphase" model that uses the same standard deviation for both modes.

In addition we conclude that there is no aggregation between the alumina and zirconia particles in this mixed dispersion. Otherwise, the theoretical attenuation based on the superposition assumption would not fit experimental data.

The situation with the second mixture (PCC—silica) is very different. In this case the predicted attenuation provides a much worse fit than the best "multiphase" model analysis. The fitting error degrades from 8% to 17.2%.
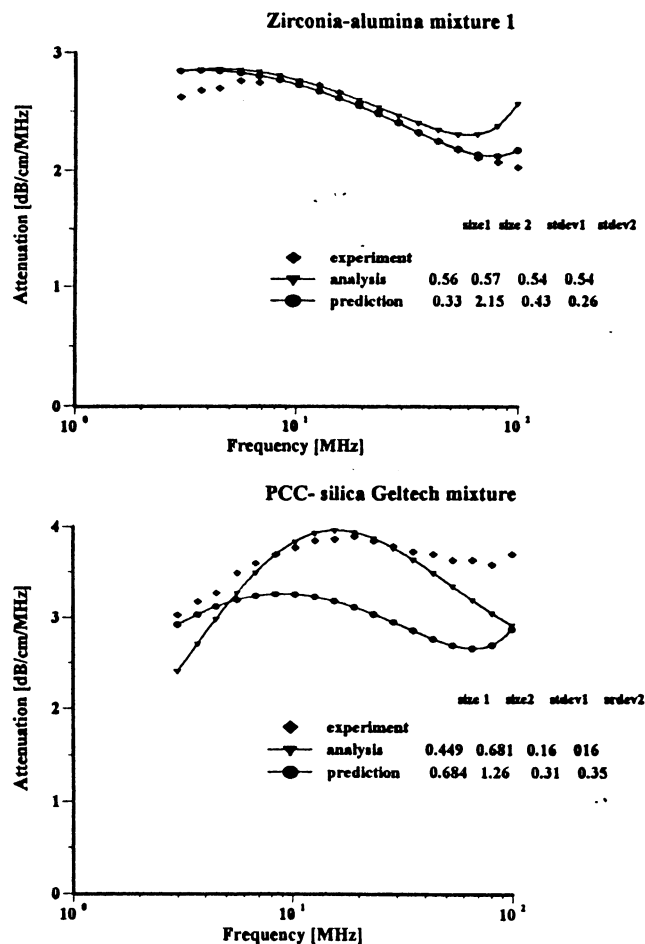

Figure 10.

In this case there is apparently some aggregation between the PCC and silica particles.

Conclusions

Acoustic spectroscopy is able to characterize the particle size distribution of dispersions with more than one dispersed phases. There are two models we can use to describe the dispersion: a "multiphase" model and an "effective medium" model.

The "multiphase" model describes the total distribution as a number of separate log-normal distributions, one for each disperse phase. Although this provides a complete description of the system, it also entails certain risks of multiple solutions because of the large number of adjustable parameters. For this reason we assumed here that the width for each mode of our binary mixtures was the same. This assumption might lead in some cases to an incorrect solution, especially when dealing with mixture of dispersed phases with widely different standard deviations.

The "effective medium model" is not complicated with multiple solution problems. It requires only two adjustable parameters for characterizing the log-normal distribution of the selected dispersed phase. All other components of mixed dispersion are considered as a new homogeneous "effective medium". We assume that attenuation of this "effective medium" is the same as measured for this mixed material separately. In those case where this assumption is valid, the "effective medium" model yields robust and reliable PSD for the selected dispersed phase. In the

PSD that differs from the expected particle size of this dispersed phase. Observation of this difference can be used as an indication of the particles interaction between "effective medium" and selected dispersed phase.

In addition to the particle size distribution, acoustic attenuation spectroscopy is able to indicate the presence of particles aggregation. To perform this test we need to calculate the attenuation spectra for PSD that is built from the individual particle size distribution by utilizing the superposition assumption. Failure of this theoretical attenuation to fit experimental data is the indication of the particles aggregation.

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