Characterization of dispersions by ultrasound spectroscopy

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In this work, a review of our main theoretical and experimental results in particle sizing of colloidal dispersions using ultrasound spectroscopy is given, with special emphasis on polymeric materials. Both low and high-concentration systems are analyzed. In the first case, a single particle literature model is shortly presented and the key problem of model parameter evaluation is addressed. With this respect, a specific approach to the direct evaluation of the intrinsic attenuation of bulk, solid materials is also mentioned. For high concentration systems, a semi-empirical modeling approach is described and validated by comparison with experimental data. A few conclusive remarks and perspectives are finally given.

Keywords: ultrasound spectroscopy, dispersion, emulsion, particle size, polymer latexes

1 INTRODUCTION

Among the different ultrasonic techniques used to characterize particle dispersions, ultrasound spectroscopy (US) shows a large potential because of two main reasons: (i) the ability to penetrate opaque systems (i.e. at high concentration) and (ii) the ability to cover huge range of particle diameter, virtually from tens of nanometers to millimeters. Both aspects are very promising with respect to on-line applications to processes where the control of the particle size is important.

The measurement principle is based on the different sound attenuation exhibited by waves at different frequency values when traveling through dispersion containing particles at various sizes. Thus, by measuring sound energy loss at multiple frequency values (so called attenuation spectrum), the size distribution of the particles can be estimated. A modeling tool is essential to properly extract the particle size and different models, suitable for different conditions, are available to this aim.

While different commercial equipments appeared in the last years, full validation of the technique is still missing, in particular with reference to popular dispersions like those involving polymer particles. In this presentation, we focus on the application of US to sizing different aqueous dispersions of spherical particles or droplets made of inorganic (silica) and organic materials (oils, polymers). In all cases, the particle diameter was in the range from 0.1 to 1 μm, thus limiting the analysis to colloidal dispersions. Different modeling approaches suitable for diluted and concentrated systems are shortly presented and validated by comparison with experimental data.

2 DILUTED SYSTEMS

2.1 Modeling

The propagation of sound waves through heterogeneous media is characterized by changes in amplitude and phase of the wave due to scattering and irreversible energy dissipation. While scattering is fully equivalent to that of light (lossless redirection), the irreversible dissipation is due to different mechanisms, mainly intrinsic, viscoinertial and thermal. Intrinsic losses are due to molecular interactions and, therefore, are always present, even in homogeneous systems. When dealing with heterogeneous systems, the discontinuity between suspending and suspended phases results in additional dissipations, related to particle vibrations (viscoinertial losses) and temperature-pressure coupling (thermal losses). A comprehensive theory accounting for these dissipation mechanisms was proposed by Epstein and Carhart for liquid-liquid systems [1] and extended to solid-liquid systems by Allegra and Hawley [2]. Such a model (below indicated as ECAH model) is used here because of its generality.

The model development can be summarized as follows: (i) wave equations are derived from the conservation laws of mass, momentum and energy; (ii) these equations are solved analytically as an infinite series of spherical Bessel functions, Legendre polynomials and unknown expansion coefficients, so-called "scattering coefficients", A_n; (iii) these coefficients can be evaluated after the introduction of the boundary conditions for the problem, i.e. the continuity of normal and tangential velocity, of normal and tangential stress and of temperature and heat flow at the interface particle phase-continuous phase. A set of linear equations can be written for each order n of the expansion coefficients; therefore, as many sets of scattering coefficients as required are independently evaluated. The complete set of equations for the coefficients is omitted here; full details can be found in the original references [2].

From the scattering coefficients, the wavenumber

characteristic of the whole dispersion, K, is readily evaluated. It is defined as $\omega/c_{eff} + i\alpha_{eff}$, being ω the angular frequency of sound and c_{eff} and α_{eff} the "effective" sound speed and attenuation of the dispersion. The relationship for K in terms of scattering coefficients is as follows:

$$\left(\frac{K}{k}\right)^2 = 1 - \frac{24i\phi}{k^3 d^3} \sum_{n=0}^{\infty} (2n+1)A_n \quad (1)$$

where k is the wavenumber of the continuous phase, ϕ the volume fraction of the dispersed phase and d the particle diameter. While the first few coefficients are required for small particles (<1 μm), large numbers of them might be required for large particles (>> 1 μm). Eq.(1) is intended for isolated particles, therefore can be applied to dilute dispersions, where the volume fraction of the dispersed phase is not larger than few percents for high the density contrast case (large density difference between the two phases) and around 20% for low density contrast case.

Eq.(1) is intended for a single value of the particle size. In the general case of particle size distribution, based on the linearity of the acoustic field, the corresponding expression of the dispersion wavenumber is readily obtained by superimposing the contributions of each particle size weighted according to their concentration. Then, Eq.(1) becomes:

$$\left(\frac{K}{k}\right)^2 = 1 - \frac{24i\phi}{k^3} \int_0^{\infty} \frac{F(d)}{d^3} \sum_{n=0}^{\infty} (2n+1)A_n(d)dd \quad (2)$$

where $F(d)$ indicates the probability density of having particles in the size range from d to $d+dd$. Such probability density function is normalized to unity and different model distributions (such as Gamma and log-normal) are usually adopted, the characteristic parameters of which are estimated by fitting the experimental attenuation data.

The equations for the scattering coefficients involve several physical properties of both continuous and dispersed phase: density, shear viscosity (liquids) or modulus (solids), speed of sound, intrinsic attenuation, heat capacity, thermal conductivity and thermal expansion. This means that accurate values of seven properties have to be known for each phase to calculate the overall wavenumber. While such properties are usually well known for the continuous, liquid phase (water in all our cases), their evaluation can be quite demanding in case of the dispersed phase and, in particular, of polymers. Actually, this evaluation problem could be a major limitation with respect to the reliability of the technique when used for sizing.

With this respect, a sensitivity analysis could be always carried out to estimate the impact of parameter uncertainties on the reliability of the model predictions. Accordingly, a smaller number of key parameters is usually identified and direct evaluation of the most important ones could be also a reasonable option, as it will be shown in the next section.

2.2 Applications

Different examples of particle sizing using US are now shown with reference to diluted dispersion of different materials. More specifically, particle size distribution, $F(d)$ (i.e. the corresponding characteristic parameters, average size and distribution broadening) and, occasionally, particle concentration, ϕ are evaluated from attenuation spectra (attenuation vs. frequency) using the model presented above. All measurements of sound absorption were carried out using the commercial equipment Ultrasizer (Malvern Ltd, UK), covering the frequency range from 1 to 100 MHz.

Silica in water [3]. This is an example of a system characterized by large density contrast. Under this conditions, and if small particles are considered, the attenuation is expected to be fully dominated by the viscoinertial mechanism, i.e. coefficient A_1 in Eq.(1). Particles in the size range from 0.1 to 0.5 μm were analyzed, always under highly diluted conditions (solid weight fraction around 1%). The results are summarized in Table 1 in terms of median diameter, d_{50}, and standard deviation, σ. Notably, different sizing techniques have been compared: electron microscopy (SEM/TEM) and dynamic light scattering (DLS/PCS). Keeping in mind that comparative analyses of different sizing methods are always difficult (for example, the average diameter and the distribution broadening estimated by DLS/PCS are not the same as those evaluated using the two other methods), a reasonable agreement is found in the two monomodal cases being the differences below 10%. On the other hand, both US and DLS/PCS do not see the first mode in the bimodal case. In the DLS/PCS case, this is an intrinsic limitation, since large particles "obscure" small ones. However, the sizing performance of US could be largely improved by selecting different model distributions, e.g. suitable for multimodal distributions. Finally, it should be mentioned that repeated measurements were found to be quite well reproduced, thus indicating a significant robustness of the ultrasonic technique.

Polymer latexes [4] [5]. A colloidal dispersion of polymer particles in water is called latex. Many industrial polymers are produced in this form and, in some cases, this is also the final product. Several end-use properties of polymer latexes are determined by particle size and the monitoring of the size distribution during the synthesis could be an extremely helpful tool. Many polymers exhibit density values not too far from that of water, so that thermal losses (and not only viscoinertial ones),

determine the attenuation behavior of such dispersions. We analyzed by US different polymers, from high (polytetrafluoroethylene, PTFE) to medium (polyvinylchloride, PVC) and low density contrast (polystyrene, PS and polymethyl methacrylate, PMMA).

Let us focus on the PVC case. A preliminary sensitivity analysis showed that, differently from the silica case, thermal properties are also important. Examples of sizing are shown in Figure 1, where PVC latexes at three different particle diameters were considered (0.2, 0.3 and 0.5 μm). The three different attenuation spectra (experimental and calculated) and the calculated particle size distribution as well, are shown in the figure. The sizing performance is indeed satisfactory: diameter values of 0.215, 0.325, 0.508 μm and 0.202, 0.315, 0.502 μm were estimated by US and DLS, respectively.

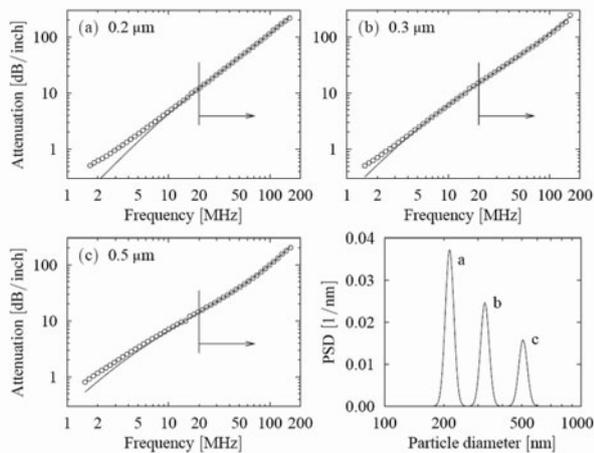Despite the good results, some discrepancies in the low frequency range (< 20 MHz) can be noticed.

Figure 1: Attenuation spectra of different PVC latexes (a = 0.2 μm; b = 0.3 μm; c = 0.5 μm) and resulting particle size distributions. Symbols are experimental data and solid curves model results. The dashed lines represent attenuation of pure water.

This behavior was actually found quite systematically, also in the case of different polymers, such as PS and PMMA. Such discrepancies were initially imputed to system "impurities" (emulsifier or residual monomer) or to gas micro-bubbles formed in-situ. However, the negligible impact of impurities was checked experimentally while careful sample treatments aimed to prevent bubble formation were not affecting the discrepancy. Then, the evaluation procedure for the different parameters was carefully reconsidered. Using the ECAH model, the different physical properties were ranked in terms of

relevance to the model predictions. Among the main parameters, the intrinsic attenuation of the polymer was identified. Such property has to be known as a function of frequency with accuracy, which is very rarely the case for polymers. Therefore, a procedure to measure directly the intrinsic attenuation of polymer slabs has been developed based on the same equipment used to measure the attenuation spectra of dispersions [5]. By using these directly measured values of the polymer attenuation, the agreement between experimental and predicted attenuation values was improved significantly with respect to the case where literature values were considered, as it is shown in Figure 2.
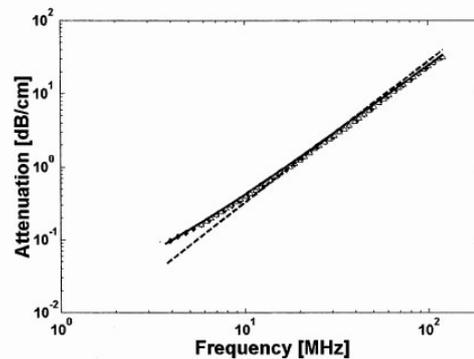

Figure 2: Attenuation spectra for PS latexes (particle diameter = 70 nm; polymer weight fraction = 0.035). Symbols are experimental data and curves model results. Solid line: measured intrinsic attenuation; dashed line: intrinsic attenuation from literature [2].

3 CONCENTRATED SYSTEMS

3.1 Modeling

One of the most attractive features of US is its applicability to high concentration, opaque systems, a decisive advantage with respect to light scattering techniques when on-line applications are considered. Even though the measurements are readily feasible, the extraction of the particle size distribution from the experimental spectra cannot be based on the model discussed above, limited to highly diluted systems. When dealing with concentrated systems, sound attenuation is exhibiting highly nonlinear dependence upon the particle concentration, a behavior not explained by Eq.(1), where linear dependence is invariably predicted. With the aim of using the same modeling framework originally proposed for isolated particles, a new semi-empirical model has been proposed for concentrated systems based on the core-shell concept [6].

The deviations from the linear dependence can be imputed to two main effects, lossless redirections due to multiple scattering and particle-particle interactions modifying the absorption mechanism at the single particle level. While the first effect has been proved to be negligible in polymer latexes [8], the second one was expected to be important

because of the very small particle separation distances typical of such colloidal dispersion at high concentration. Therefore, a core-shell model was proposed where the original polymer particle is embedded into a shell of pure continuous phase (water in our cases) which is in turn immersed in a kind of "effective medium". Being the system description still based on a single particle, the same fundamental conservation laws of the ECAH model were adapted and analytically solved. However, the introduction of a third phase causes the number of scattering coefficients to increase from 6 to 12 for each n value. Again, these coefficients need to be evaluated in order to compute the attenuation of the dispersion using Eq. 3:

$$\alpha_{eff} = -\frac{12\phi}{k^2 d^3} \sum_{n=0}^{\infty} (2n+1)\text{Re}(A_n") + \alpha_B \qquad (3)$$

where α_B is the background attenuation (volume-average of the intrinsic attenuations of continuous and dispersed phase) and $A_n"$ are the scattering coefficients characterizing the waves leaving the particle surface inside the shell, those affecting the measured total attenuation. This equation, originally proposed in the literature for diluted systems [1] [2], was used instead of the more comprehensive Eq.(1) because of its improved numerical stability [6].

Finally, the evaluation of the additional quantities of the core-shell model with respect to the original single-particle model deserves few comments. The size of the shell has been evaluated as a function of the particle concentration so as to fill the free, interparticle space. Therefore, it is a given function of the particle diameter when the particle concentration is known. Moreover, the values of the physical properties of the fictitious, effective medium have been estimated as volume average of the properties of the original phases, with the exception of viscosity, which is always assumed the same as that of the continuous phase. Despite the large empiricism involved in this choice, this approach resulted quite effective for most examined systems, as it is shown in the next section.

3.2 Applications

The core-shell model has been validated by sizing different aqueous dispersions of solid particles (silica and polytetrafluoroethylene, PTFE) and droplets (corn oil) [7]. The case of PTFE is shown in Figure 3.

The significant improvement introduced by the core-shell approach is quite evident and the nonlinear dependence of the attenuation upon the particle concentration is properly predicted. The sizing performance of the two models is compared in Figure 4, where the size predictions for all mentioned systems are compared. The core-shell model is clearly suppressing the drift with

concentration of the predicted particle size, a clear artifact introduced by the ECAH model when applied to concentrated systems.
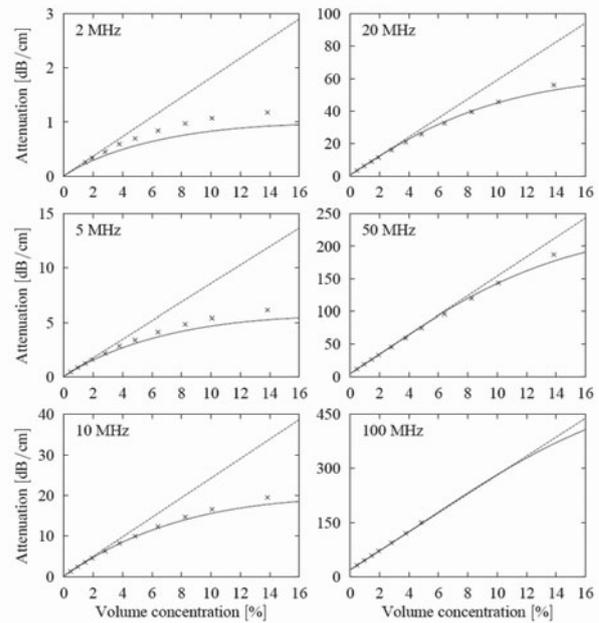

Figure 3: Attenuation vs. particle volume concentration for a PTFE latex (particle diameter 0.2 μm) at different frequency values. Solid line: core-shell model; dashed line: ECAH model.
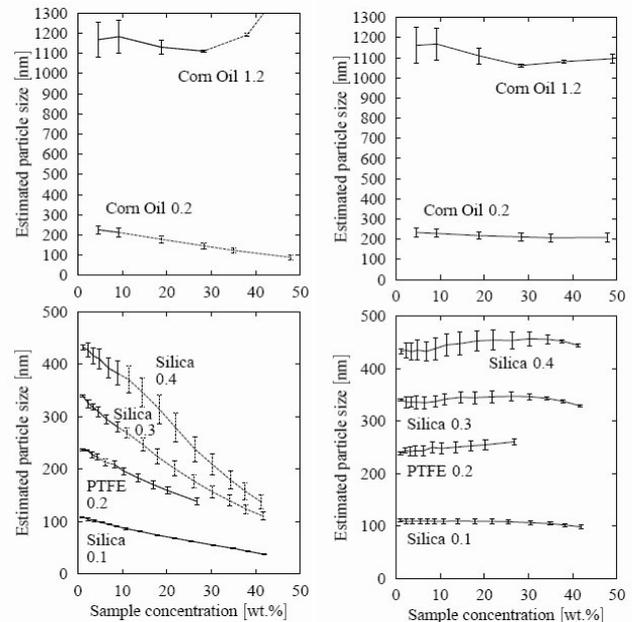

Figure 4: Particle sizing using ECAH model (left) and core-shell model (right). Average particle diameter and distribution variance were predicted at given particle concentration (numbers indicate the approximate average diameter in μm).

4 CONCLUDING REMARKS

The reliability of the particle sizing based on sound attenuation measurements has been explored with reference to solid-liquid and liquid-liquid dispersions. Even though different models covering remarkably large ranges of concentration are available, the evaluation of the many required physical properties could be a significant limitation. This is even all the more true when analyzing systems containing materials the properties of which are not well defined or changing in time due to reaction processes. A sensitivity analysis of the model predictions with respect to such parameters was found quite helpful in ranking them according to their relevance with respect to sizing and, therefore, to identify the required accuracy of the corresponding value.

Even though colloidal dispersions (submicron particle diameters) were analyzed in this work, the same technique and the same modeling tools can be applied to systems involving larger particles. Examples in this direction are given in the literature with reference to the monitoring of crystallization processes (crystal size around 100 μm, [9]) and of three-phase gas-liquid-liquid systems (droplet size around 100 μm, gas bubble size around 1 mm, [10]).

Finally, it could be mentioned that further advances in the equipment technology are continuously appearing towards the miniaturization of the apparatus and, in particular, of the measuring cell. Such advances could open major perspectives with respect to on-line applications for process monitoring where the quality control of particulate products is the main requirement.

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Table 1: Comparison of sizing results on aqueous dispersions of silica using ultrasound spectroscopy (US), microscopy (SEM/TEM) and light scattering (DLS/PCS) (from [3]).

	US	TEM/SEM	DLS/PCS
Silica 0.1 μm			
d_{50} (PCS: d_{PCS}) (nm)	82	81	112
σ (PCS: Pd)	0.09	0.19	0.10
Silica 0.3 μm			
d_{50} (PCS: d_{PCS}) (nm)	314	346/354	355
σ (PCS: Pd)	0.05	0.05	0.06
Silica 0.2/0.5 μm (bimodal)			
D_{50} (PCS: d_{PCS}) (nm)	432	215/483	419
σ (PCS: Pd)	0.05	0.18/0.22	0.16