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Application of ultrasound spectroscopy for nanoparticle sizing in high concentration suspensions: A factor analysis on the effects of concentration and frequency

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ABSTRACT

Ultrasound is an attractive technique for nanoparticle sizing as it offers non-invasive, suitable for highly turbid and concentrated samples, and potentially no sample dilution needed features. This paper presents a factor analysis method for the determination of the concentration range and frequency domain for the use of ultrasound techniques for particle sizing when ECAH (Epstein, Carhart, Allegra and Hawley) model is applied. The advantage of using this method is by dealing with experimental data, some practically useful information, which the current theory cannot be employed to produce, may be identified, for instance, the critical volume concentration of particles below which sound attenuation is linearly dependent on particle concentration and the frequency domain in which frequencies have higher contribution to the attenuation than those outside the domain.

To use this method, each data matrix is constructed by ultrasound attenuation data with frequency as variables and concentration as observations. Attenuation data are obtained with the measurements of ultrasound spectroscopy of oil/water emulsions and solid/water suspensions at different concentrations.

As a result of the factor analysis, for emulsions up to 40%vol concentration, the linear dependence of attenuation on concentration and a same level contribution of frequency ranging from 1 to 120 MHz are found. However, for solid suspensions, attenuation appears to be nonlinearly related to solid concentration and the critical concentration value at which attenuation is turning into nonlinear from a linear trend can also be calculated. It is also found that in solid suspensions, frequencies less than 10 MHz have less contribution to attenuation than that of higher than 10 MHz. Therefore, for ultrasound particle sizing using ECAH model, before the inversion of attenuation to particle size distribution takes place, using this method the range of concentration and frequency to which the use of ECAH model is valid can be determined.

1. Introduction

Manufacture of micron/nanometre particulate products in high solid concentration suspensions is becoming increasingly important to pharmaceutical, agrochemical and speciality chemical industries. In these applications, the particle size and size distribution are critical properties as they affect the final suspension stability, particle solubility, bioavailability and even toxicity of drugs.

Often industrial scale operation needs to be at high concentrations and measuring samples at their original concentrations is critical, this poses great challenges to particle size measurement and consequently to the control of the process. With ultrasound offering non-invasive, fast and potentially no sample dilution required attractions, such a technique based particle sizing is receiving great attentions from the industry world and the academic community (Dukhin et al., 1996; Dukhin and Goetz, 1996, 2002; Povey, 1997, 2000; Babick et al., 1998; Challis et al., 2005; Shukla and Prakash, 2006).

The principle of ultrasound particle sizing technique is to measure the attenuation of ultrasound in terms of frequency as acoustic waves propagate through the particle suspensions and then invert the attenuation into particle size distribution. The primary theoretical model for the inversion (Alba, 1992) is attributed to the general acoustic theory of ECAH (Epstein and Carhart, 1953; Allegra and Hawley, 1972). This ECAH model is essentially only valid for a single isolated particle immersed in an infinite medium, i.e. much diluted systems. For a system with a number of particles, the total sound attenuation caused by all the particles is calculated as the addition of the contribution from each particle. According to the ECAH theory, total attenuation caused by particles with size l in diameter and volume concentration ϕ_l is proportional to ϕ_l/l^3 (this is because according to the ECAH theory, the attenuation of sound caused by

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particles l is expressed as

$$-\frac{12}{k^2}\frac{\phi_l}{l^3}\sum_{n=0}^{\infty}(2n+1)\mathrm{Re}\,A_n$$

where k is the compression wave number, $\mathrm{Re}A_{\mathrm{n}}$ is the real part of the coefficients of Legendre polynomials). This means that the ECAH model can only be used when attenuation and concentration are linearly correlated.

Therefore, for ECAH model based ultrasound particle sizing, it is important to know up to what concentration, use of the model is valid for all the transmitted frequencies. Also, in the application of ultrasound techniques, transmitted frequency often ranges from 1 to 160 MHz (Ultrasizer User Manual, Malvern Instruments Ltd, 1998). It is thus necessary to know whether different frequencies are effectively making the same contribution to the attenuation so that the less important frequency domain due to noises such as foams and occasionally large dusts can be eliminated before the inversion in order to produce the right particle size and improve the computational efficiency. More importantly, change of frequency results in the variation of concentration point where nonlinearity starts occurring. So it is crucial to find the nonlinearity turning point for the entire applied frequency domain in order to determine the concentration range for the ECAH model to be valid. Factor analysis presented in this paper provides a method to address these issues.

Factor analysis is a statistical method (Kim and Mueller, 1978; Gorsuch, 1983; Kline, 1994; Manly, 2005) for multivariate data analysis to identify the underlying factors with whose linear combinations the observed variables can be expressed. The aim of this analysis is to summarise the inter relations among those variables. It should be mentioned at this stage that the concerned variables are the sound frequencies and the observed values are the attenuations measured at different frequencies and particle concentrations.

Typically, there are two types of factor analyses: exploratory and confirmatory. The former is to explore the main structure or dimensions of multivariate data (Spearman, 1904). This type of factor analysis simplifies the study field by indicating what variables are more important than others in constructing a variation field and affecting results of measurements (Kline, 1994). The confirmatory analysis was developed for testing hypotheses (Popper, 1959; Joresjog, 1973). In this paper, exploratory analysis is used.

Three main steps are involved in factor analysis (Manly, 2005): first, extraction of the common factors and determination of the provisional factor loadings; second, rotation of the selected factors and finally calculation of the factor scores. Before these main steps, a covariance or correlation matrix including all the observed variables and measurements must be constructed. The covariance matrix is used when comparison of factor structures across groups is needed otherwise correlation matrix is taken into the analysis especially for those measurements with variables varying in wide metrics. In this paper, correlation matrices are constructed into analysis because the value of attenuation scales widely in terms of frequency and concentration.

There are quite a few techniques to extract the common factors and to determine the provisional factor loadings (Kim and Mueller, 1978). (I) Maximum likelihood method (Lawley, 1940; Maxwell, 1971; Joreskog, 1967; Joreskog and Lawley, 1968). (II) Least squares method (Thomson, 1934; Harman, 1976a, 1976b). (III) Alpha factoring (Kaiser and Gaffrey, 1965). (IV) Image analysis (Guttman, 1953; Harris, 1962). (V) Principal component analysis (Hotelling, 1933). The last technique will be used in this paper.

In addition to the techniques of extracting factors, rotation of factors is also critical in factor analysis as it achieves a simple structure of factors (Thurstone, 1947; Cattell, 1978) and makes the factors more interpretable. There are three main methods to do the factor rotation (Kim and Mueller, 1978; Kline, 1994): graphical (Mulaik, 1972), oblique and orthogonal. However, graphical rotation appears to be impractical as with large number of factors, the processing is tedious and lengthy (Kline, 1994) and it is unlikely that one will be able to see a simple structure of these factors. Oblique rotation (Gorsuch, 1983) may become problematic (Nunnally, 1978) when it turns out to interpret the result of rotation. For orthogonal rotation, compared with quartimax (Carroll, 1953; Sauders, 1953; Neuhaus and Wright, 1954; Ferguson, 1954) and equimax (Kim and Mueller, 1978), varimax (Kaiser, 1958) showed reasonably effective and more invariant thus has been widely accepted as the main technique for factor rotation (Kim and Mueller, 1978; Gorsuch, 1983; Kline, 1994). It is also the technique used in this paper.

2. Background theory of factor analysis

A matrix $\boldsymbol{\alpha}$, which in this paper contains the sound attenuation values at p frequencies of n independent measurements of concentrations, can be transformed into a $p\times p$ correlation matrix by removing its means and through standard deviation standardisation. With the technique of principal component analysis, p principal components $\mathbf{P}$ can be formed as the linear combinations of $\boldsymbol{\alpha}$ with a $p\times p$ coefficient matrix B. This can be expressed as

$$\mathbf{P} = B\boldsymbol{\alpha} \tag{1}$$

where the values of B are given by the eigen vectors of the correlation matrix. B is thus orthogonal and its transpose B' and inverse matrix are equal. This expression can then be transformed into

$$\boldsymbol{\alpha} = B'\mathbf{P} \tag{2}$$

For a factor analysis, only m of $\mathbf{P}$ are retained for the calculation of the unrotated factor loadings

$$\boldsymbol{\alpha} = B'_{p\times m}\mathbf{P}_m + \mathbf{E}_{p-m} \tag{3}$$

where $\mathbf{E}_{p-m}$ are the errors generated by the negligence of the $p-m$ components. It must be pointed out at this stage that the criterion to select the first m components is dependent on the rules that the analyst chooses to use such as the use of eigen value limitation (typically 1.0), number of factors or according to the percentage of the total variance of the m components possess.

All to be done now is to scale the selected m components to have unit variances as required for the m factors $\mathbf{F}_m$ by ignoring the errors. The way to do so is to divide each $\mathbf{P}$ by its standard deviation which is the squared root of the corresponding eigen value $\sqrt{\lambda}$ in the correlation matrix. This can be expressed as

$$\boldsymbol{\alpha} = A_{p\times m}\mathbf{F}_m \tag{4}$$

where

$$\mathbf{F}_m = \frac{\mathbf{P}_m}{\sqrt{\lambda_m}} \tag{5}$$

$$A_{p\times m} = B'_{p\times m}\sqrt{\lambda_m} \tag{6}$$

Column values of $A_{p\times m}$ are the corresponding unrotated factor loadings.

After a rotation, varimax or any other type, Eq. (3) is then changed to

$$\boldsymbol{\alpha} = G_{p\times m}\mathbf{F}^*_m \tag{7}$$

where $\mathbf{F}^*_m$ refers to rotated factors and $G_{p\times m}$ is the final factor loading matrix. The dot product of $G_{p\times m}$ and the score in the principal component analysis of the original correlation matrix is the new score of original variables under new factors.