Deconvolution of light-scattering patterns by observing intensity fluctuations

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Results are presented on the statistical fluctuations occurring in a forward-light-scattering experiment to determine the particle size distribution. A sample of glass beads was measured using a Malvern 2600D instrument and analyzed with a proposed deconvolution procedure that incorporates the observed intensity fluctuations. This procedure yields a qualitative improvement of the solution, provides error intervals, and offers a better means for model discrimination.

Introduction

So far, all the strategies used for deconvolution in forward-light-scattering experiments to measure particle size distributions (PSD's) are based on a comparison between a light-scattering model, which contains a set of calculated light intensity patterns, and the mean values of the recorded intensity pattern. To reconstruct the PSD that causes this pattern, an inversion algorithm is applied based on either matrix inversion, integral transformation, or a combination of both. The success of the deconvolution procedure depends on the type of inversion technique employed and a proper choice of the parameters to describe the recorded light-scattering pattern contained in the model matrix.

We discuss a model-independent deconvolution procedure based on an inversion scheme. Model-independent deconvolution means that no assumptions are made beforehand about the shape of the PSD as is done for normal, lognormal, Rosin–Rammler, and other types of distribution. This procedure incorporates the mean scattered intensity and its standard deviation. The reasons for developing this procedure were to enhance the stability, reliability, and resolution of the deconvolution step and to obtain confidence intervals for the resulting PSD. Also a better understanding of the effects of measurement time, concentration, and model matrix on the derived size distribution was pursued. The instrument used to record the scattering patterns was a Malvern 2600D particle sizer, equipped with a 5-mW He–Ne laser (λ = 632.8 nm) with a beamwidth of 9 mm. The optical arrangement of the instrument is depicted in Fig. 1.

In a forward-light-scattering experiment all particles present in the optical measuring volume at time t will contribute to the scattering pattern received by the photodiode array detector during readout. The size of this volume is set by the width of the incident laser beam and the path length between the optical windows of the sample cell. The collecting transform lens mounted behind the sample cell focuses all individual scattering patterns onto the detector. The Malvern 2600D detector consists of 31 semicircular rings n. An additional detector in the center is used to align the laser and measures the transmission by collecting the unscattered incident light. The detection angle covered by each ring is a function of its radial position and the focal length f of the collecting lens. A more detailed description of the instrument, including the dimensions of the detector rings is given by Hirleman et al. One readout of all successive detector rings is henceforth referred to as a sweep. The final recording after a sweep contains an integrated intensity pattern, or energy pattern, which is then digitized by a 10-bit analog-to-digital converter and subsequently stored in the computer.

Symbols and Abbreviations

- a is the element of scattering model matrix A;
- A is the scattering model matrix (n x m);
- A^T is the transpose of A (m x n);
- A^w is the weighted A (n x m);
- cov is the covariance matrix n x n or m x m;
- df is the degrees of freedom;
- f is the focal length of the collecting lens.
Fig. 1. Optical arrangement of the forward-light-scattering technique.

\[
\begin{align*}
\mathbf{H} & \text{ is the smoothing matrix } (m \times m); \\
i & \text{ is the counter of } n; \\
j & \text{ is the counter of } m; \\
k & \text{ is the sweep number; } \\
\mathbf{L} & \text{ is the integrated light intensity vector } (n); \\
\mathbf{L}_i & \text{ is the calculated } L(n); \\
m & \text{ is the number of size classes; } \\
n & \text{ is the number of detector rings; } \\
q & \text{ is the fractions of PSD } (m); \\
s & \text{ is the total number of sweeps; } \\
t & \text{ is the time; } \\
\gamma & \text{ is the smoothing scalar; } \\
\epsilon & \text{ is the random measurement error } (n); \\
\lambda & \text{ is the wavelength of the incident illuminating source; } \\
\mu & \text{ is the expected mean value of } \langle \cdot \rangle; \\
\nu & \text{ is the unbiased estimator of } \mu; \\
\sigma & \text{ is the expected standard deviation of } \langle \cdot \rangle; \\
\delta & \text{ is the unbiased estimator of } \sigma; \\
\sigma^2 & \text{ is the expected variance of } \langle \cdot \rangle; \\
\chi^2 & \text{ is the reduced sum of the squares of the residuals.}
\end{align*}
\]

Model-Independent Deconvolution by Direct Inversion

If the contributing particles are divided into \( m \) discrete size classes, the recorded scattering pattern can be written as a set of linear equations:

\[
\begin{bmatrix}
L_1 \\
L_2 \\
\vdots \\
L_m
\end{bmatrix} = \begin{bmatrix}
a_{11} & a_{12} & \ldots & a_{1m} \\
a_{21} & a_{22} & \ldots & a_{2m} \\
\vdots & \vdots & \ddots & \vdots \\
a_{m1} & a_{m2} & \ldots & a_{mm}
\end{bmatrix} \begin{bmatrix}
q_1 \\
q_2 \\
\vdots \\
q_m
\end{bmatrix} + \begin{bmatrix}
\epsilon_1 \\
\epsilon_2 \\
\vdots \\
\epsilon_m
\end{bmatrix}
\]  

(1)

In vector notation this reads

\[\mathbf{L} = \mathbf{Aq} + \epsilon,\]

(2)

where \( \mathbf{L} \) is the vector of the integrated light intensity versus scattering angle, \( \mathbf{A} \) is the scattering matrix, which contains the scattering coefficients \( a_{ij} \) calculated according to the scattering function employed (e.g., Fraunhofer, anomalous diffraction, or Lorenz-Mie), \( \mathbf{q} \) is the solution vector, which contains the fraction of particles in each size class, and \( \epsilon \) represents the random measurement error on \( \mathbf{L} \).

The least-squares solution of \( \mathbf{q} \) is obtained by direct inversion of the set of linear equations. With \( n \geq m \) the least-squares estimators for \( \mathbf{q} \) are given by

\[\mathbf{q} = (\mathbf{A}^T\mathbf{A})^{-1}\mathbf{A}^T\mathbf{L}.\]

However, deconvolution by direct inversion often fails because of the measurement errors included in \( \mathbf{L} \) and systematic errors contained in the scattering model matrix \( \mathbf{A} \). Without stabilizing the set of equations the solution is subject to severe oscillations and may yield negative equivalent fractions for some elements of \( \mathbf{q} \).

Phillips–Twomey Inversion

The oscillatory behavior of the solution vector can be suppressed by adding an additional \( m \times m \) matrix, which is referred to as the Phillips–Twomey approach. This matrix \( \mathbf{H} \) serves as a smoothing matrix, as it effectively links the elements of \( \mathbf{q} \) by their second-order differences. A smoothing scalar \( \gamma \) determines the extent of smoothing incorporated in the final solution:

\[\mathbf{q} = (\mathbf{A}^T\mathbf{A} + \gamma\mathbf{H})^{-1}\mathbf{A}^T\mathbf{L}.\]

The optimal choice of \( \gamma \) is left to the interpretation of the user and is in practice determined by trial and error. The selected value is then used for a whole range of subsequent measurements, for example, in the case of on-line process control. Furthermore its absolute value depends on the coefficients included in...
the model matrix $A$, which is often arbitrarily scaled. Inconsistent scaling makes a comparison with previous work irrelevant. The advantage of this modified model matrix inversion step is its speed compared with iterative procedures. The main drawback is the inclusion of smoothing in $q$, particularly for narrow size distributions. Examples of this method are presented by Chow and Tien, Caroon and Borman, and Heuer and Leschonski. To eliminate the effects of smoothing and at the same time enhance both speed and stability, another method of direct model matrix inversion was designed.

Incorporation of Fluctuations

When a measurement is performed a number of sweeps $s$ is recorded and stored in a computer. The successively recorded scattered patterns will all be slightly different. The extent of the fluctuations observed between these patterns will vary for each detector ring. This is caused by

1. statistical variations between the fractions of the PSD contained in the optical measuring volume for successive recordings;
2. concentration effects due to local inhomogenities of the dispersion;
3. nonsphericity of the particles examined, which leads to different scattering signatures for the same particle depending on its orientation in the optical measuring volume;
4. instability of the incident laser intensity;
5. noise introduced by the detector.

These fluctuations cause a sweep-to-sweep variability, which is quantified before entering the deconvolution step. This is done by comparing the light energy values for all individual sweeps on each ring. It is assumed that the fluctuations follow a normal or Gaussian distribution. Then the values on all rings are characterized by an estimator of the expected value for their mean $\mu$ and variance $\sigma^2$ as follows:

$$\mu_i = \left( \sum_{t=1}^{s} L_{i,t} \right) / s, \quad (5)$$
$$\sigma^2 = \left[ \sum_{t=1}^{s} (L_{i,t} - \mu_i)^2 \right] / (s - 1). \quad (6)$$

A further characterization is the degree of association that exists between the individual detector rings during the measurement. The covariance matrix is constructed by comparing all sweeps on ring $i$ with those on ring $j$:

$$\hat{\sigma}_{ij} = \left[ \sum_{t=1}^{s} (L_{i,t} - \mu_i) \cdot (L_{j,t} - \mu_j) \right] / (s - 1). \quad (7)$$

The covariance matrix of $L$ can be rewritten into its cross-correlation matrix:

$$\rho_{ij} = \hat{\sigma}_{ij} / (\hat{\sigma}_i \hat{\sigma}_j)^{1/2}. \quad (8)$$

Next the equation for the least-squares solution is weighted for the observed spread, dividing both light energy vector $L$ and model matrix $A$ by the calculated total standard deviations. A background measurement is performed before particles have entered the optical measuring volume and serves to study the fluctuations caused by the laser, light from the surroundings, and the detector itself. The variance of the measurement is much larger than the variance of the background, which is added as a correction term. Since both variances are caused by random errors, the total variance may be expressed as the sum of the variances observed for the background measurement $(bg)$ and the sample measurement $(sm)$:

$$\sigma_{sm}^2 = \sigma_{bg}^2 + \sigma_{sm}^2. \quad (9)$$

Weighting yields

$$L_i = L_i / \sigma_{sm}^2, \quad (10)$$
$$a_q = a_q / \sigma_{sm}^2. \quad (11)$$

Then the modified equation becomes

$$q = (A^T A)^{-1} A^T L. \quad (12)$$

The purpose of weighting is to take into account the differences in measurement error between each ring. Added to this is a nonnegativity constraint, which greatly helps to stabilize the solution, i.e., to avoid any singularity in the $A^T A$ matrix. In the algorithm used here, we implemented Eq. (12). If there were negative elements in $q$, the relevant row in model matrix $A$ was eliminated and the equation was applied again. This procedure was repeated until only positive elements were obtained and the conditions for the Kuhn-Tucker theorem were fulfilled. The procedure converges to the same solution independent of the starting values.

After deconvolution the standard errors of the least-squares estimators of solution vector $q$ can be studied. Recall that we have assumed Gaussian statistics to construct the covariance matrix of the light energy pattern. This means that the variance of $q$ can be directly derived from its weighted least-squares solution given in Eq. (12):

$$\text{cov}(q) = \text{cov}((A^T A)^{-1} A^T L), \quad (13)$$
$$\text{cov}(q) = (A^T A)^{-1} A^T \text{cov}(L) A (A^T A)^{-1}. \quad (14)$$

If the cross correlation between the rings is negligible, for fraction $q_j$ the above reduces to

$$\text{cov}(q_j) = (A^T A)^{-1} \chi_{n,m}^2, \quad (15)$$

where

$$\chi_{n,m}^2 = \left[ \sum_{t=1}^{s} (L_i - L_{i,j})^2 \right] / df, \quad (16)$$

and $df = (n - m)$ is the number of degrees of freedom.
and \( L = Aq \) is the calculated energy pattern after deconvolution.

The absolute value of the reduced chi-square (\( \chi^2_{\text{red}} \)) indicates whether the deconvolution has been successful. If \( \chi^2_{\text{red}} \) is unsatisfactorily large, its profile of residuals indicates the position of the detector rings with the most serious deviations. In that case another model matrix should be employed.

**Results and Discussion**

The concept of observing scattered intensity fluctuations is illustrated. A sample of glass beads dispersed in water was analyzed with the Malvern 2600D. Glass beads are essentially spherical particles, and so disturbances of the scattering pattern because of different orientations of the particles are eliminated. The following relative refractive index was used to describe the glass beads in water: \((1.55 - 0.0i)/1.33\). The obscuration of the incident laser beam because of light scattered by the particles in the optical volume was 25%. The focal length of the lens used in the experiment was 100 mm, covering an angular range from 0.1 to 8.1 deg. During the experiment 1000 sweeps were recorded at a sampling rate of 6.37 Hz (157 ms/sweep). The 31st detector ring (outermost) was not used.

Figure 2 shows the scattered-light energy data collected by five detector rings or channels where a lower channel number denotes a lower scattering angle. Autocorrelation on the data of all channels indicated that no relationship exists between the successive sweeps and that the collected data are randomly distributed around an average value. The bandwidth of scattering data around the average value depends on the channel number. This is again illustrated in Fig. 3 where the data for the five channels of Fig. 2 are sorted, showing that the distribution of light energy values is reasonably Gaussian. Figure 4 shows the average scattering pattern caused by the particles and the average background pattern taken before the measurement.

Deconvolution of the average recorded pattern depicted in Fig. 4 is performed with a model matrix based on the appropriate relative refractive index.

\[
a = 10^{a(0-20)},
\]

where \( a \) is the lower size limit, \( j \) refers to the \( j \)th size class, and \( b \) sets the number of size classes per decade with multiples of 20. The solution for the amount of particles contained in each size class is expressed as an equivalent volume fraction. The overall lower and upper size limits for the deconvolution were set to 1.0 and 125.9 mm, respectively.

In Fig. 5 the quality of the fit, expressed as the reduced chi-square, is plotted against the number of size classes derived following the proposed deconvolution routine. The best fit is obtained around 20 size classes or 10 degrees of freedom. Figure 6 gives the size distributions for both the proposed (solid bars) and the Phillips–Twomey (dashed bars) methods of deconvolution for 21 size classes. It shows that the Phillips–Twomey method, by linking the size classes by their second-order differences, is unable to respond to rapid changes in the size distribution, which results in a smooth and symmetrical solution. The
value of $\gamma$ selected yielded the smallest $\chi^2_{\text{red}}$. It is clear from the profiles of the residuals (Fig. 7) that the smoothing forces the calculated scattered-light energy pattern to deviate significantly more from the measured pattern than for the proposed method, which treats all size classes of the solution independently. As a last step of the proposed deconvolution method, standard errors for all size classes are derived based on the observed fluctuations. These intervals are represented by the dashed bars in Fig. 8. Finally Fig. 9 gives an indication of the computing time needed to reach convergence as a function of the number of size classes obtained based on an 8-MHz AT with a mathematical coprocessor.

Conclusions
The inclusion of information on the intensity fluctuations offers an additional possibility of enhancing the deconvolution step in forward light scattering. This is achieved by expressing the observed fluctuations as variances and using them to weight the equation of the least-squares solution accordingly. Based on this concept a model-independent inversion procedure has been presented. An increase in stability of the linear set of equations is achieved by the nonnegativity constraint rather than by adding smoothing. From the profile of residuals an indication is presented about the applicability of the model matrix applied to

Fig. 5. To locate the best solution of the scattering pattern given in Fig. 4, the reduced $\chi^2$, derived after deconvolution with the proposed method, is plotted as a function of the number of size classes.

Fig. 8. Standard error intervals (dashed bars) obtained with the proposed method of deconvolution for the solution (solid bars) presented in Fig. 6 based on the observed fluctuations for all channels.

Fig. 9. Computing time needed to reach the convergence as a function of the number of size classes derived from the scattering pattern presented in Fig. 4 with the proposed method of deconvolution. Data are based on an 8-MHz AT with a mathematical coprocessor.
describe the measurement. After deconvolution an estimate of the accuracy of the solution is obtained. The ability to estimate error intervals is especially important for the control of processes in which particles are involved, e.g., crystallization. A further step is to implement the complete covariance matrix of the light intensity vector and to predict confidence intervals of the size distribution as a function of resolution.

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