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Particle sizing by laser diffraction spectrometry in the anomalous regime

Karl A. Kusters, Johan G. Wijers, and Dirk Thoenes

The application of laser diffraction spectrometry to determine the size distributions of particles in the anomalous diffraction regime, i.e., particles with a refractive-index ratio close to one, has been examined. From a computer simulation, using the Mie theory and the geometrical optics approximation, it could be concluded that for suspensions with a refractive-index ratio near 1, the corresponding scattering matrix is required for calculation of the correct particle size distribution, even in the case of particles that are much larger than the wavelength of the incident light. In a system with the refractive-index ratio almost at unity, a suspension of ice crystals in a sucrose solution, the ice particles were sized by means of optical microscopy and laser diffraction spectrometry, and the results were compared.

Key words: Laser diffraction particle sizing, anomalous diffraction, particle sizing errors associated with the Fraunhofer diffraction assumption, scattering matrix, geometrical optics approximation, optical microscopy, sizing of ice crystals in aqueous solutions.

I. Introduction
Forward lobe light scattering offers a powerful noninvasive technique for the size analysis of particulate suspensions. Unlike other optical techniques, laser diffraction spectrometry does not require single particles to be measured successively to obtain a size distribution. Instead the interaction between light and the ensemble of all illuminated particles is analyzed. Analysis is rapid and makes on-line measurements possible. This technique is particularly useful for studying crystallization, aggregation, and dispersion phenomena.

The exact description of light scattering by spherical isotropic particles is given by the Mie solution of the Maxwell equations for electromagnetic radiation. In the submicrometer range, i.e., for particles smaller than the wavelength \( \lambda \) of light, it is claimed that the Mie theory is required for an adequate description of the forward-scattering patterns. For particles with a diameter \( x \) larger than the wavelength \( \lambda \), Fraunhofer diffraction is often assumed. However, only scattering by opaque particles or particles with a large real refractive-index ratio \( m \), i.e., the ratio of the refractive index of scattering particles to that of the fluid, results in diffraction patterns that are adequately described by Fraunhofer diffraction theory. For a system that gives rise to anomalous diffraction, i.e., a system that consists of particles that are large with respect to the wavelength of light and with \( m \) close to 1, the refraction of light through the particle contributes considerably to forward scattering.

This work was aimed at quantifying the errors that occur when this refraction is ignored, and the laser diffraction apparatus is applied to systems for which it is not calibrated. To evaluate these errors we simulated the scattering of particles with different relative refractive indices \( m \) and several size distributions. From the computed light energy distribution the particle size distribution was calculated using the standard scattering matrix with which the laser diffraction apparatus has been equipped. The computed particle size distribution is compared with the original one.

We also performed some laser diffraction measurements in a suspension of ice crystals in a sucrose solution, a system with a refractive-index ratio near 1. The measured scattering patterns were processed with the standard matrix and with the matrix especially computed for this particulate system with the corresponding refractive-index ratio. The ice particles were also sized using optical microscopy. The results are compared with those obtained by laser diffraction spectrometry.
II. Principle of Forward Laser Light Scattering

The measurement of scattering patterns was carried out by means of a Malvern 2600 particle sizer. The optical arrangement is shown schematically in Fig. 1. Particles are allowed to move across a parallel laser beam. The scattered light is focused by a Fourier transform lens onto 30 semicircular photosensitive rings placed at predetermined radii in the detector plane. The annular rings are approximately log spaced, and the dimensions of the detector are listed by Dodge and Hirleman. The particle sizer is equipped with six lenses with corresponding size ranges as shown in Table I. The size classes used in the laser diffraction instrument are defined by the detector dimensions and focal length through the relation:

\[ x(i) = \frac{\lambda}{\pi \sin[\arctan(r(i)/FL)]} \times 1.357, \quad (1) \]

where \( \lambda \) is the wavelength of He–Ne light in vacuum = 0.6328 \( \mu \)m, \( r(i) \) is the distance of the detector element \( i \) from the center of the detector, \( x(i) \) is the particle size representing the \( i \)th size class, and \( FL \) is the focal length of the Fourier-transform lens.

If successive detector elements are united into pairs, we arrive at 15 size classes for each lens. A 16th size class comprises all particle sizes smaller than the lower limit of the 15th size class.

Each detector ring effectively measures the energy of the scattered light at a particular angle to the incident beam. The particle size distribution is then inferred through a mathematical procedure that attempts to match the measured and calculated energy distributions over the detector rings. A brief description of the fitting procedure used by the Malvern 2600 particle sizer is given in Appendix A. The fitting procedure is a model-independent iterative technique; i.e., it does not constrain the volume distribution to follow a common analytic expression, such as the two-parameter Rosin–Rammler or the lognormal distribution functions. The fitting error, which is being minimized, is the logarithm of the sum of the squared differences between the measured and calculated light energy patterns. When the measured and calculated light energy patterns are normalized so that their peak values are equal to 2047, a good fit is obtained if the fitting error is \( \leq 4 \). The deconvolution problem can be written as a set of linear equations expressed in matrix notation as

\[ L = A \cdot Q. \quad (2) \]

where \( L \) is the light energy vector, \( Q \) is the particle size volume distribution vector, and \( A \) is the scattering matrix.

The total light energy measured on a detector ring is developed from the contributions of all the particle sizes present. Only the amount of this contribution varies with size. This information is stored in the scattering matrix \( A \). The scattering matrix has 15 rows (15 detector element pairs) and 16 columns (16 size classes). Matrix coefficient \( a(i,j) \) represents the light energy on the adjacent detector elements \( 2i - 1 \) and \( 2i \), scattered by size class \( j \) and normalized on a volume basis:

\[ a(i,j) = l(i,j)/x(j)^2, \quad (3) \]

where \( l(i,j) \) is the light energy scattered by the size class \( j \) on the detector elements \( 2i - 1 \) and \( 2i \).

The fitting procedure assumes uniform weighting on a volume basis within each size class.

The scattering matrix is dependent on two parameters:

1. The choice of a focusing lens, which fixes the particle size range and particle size classes.
2. A relative refractive index of the scattering particles.

The Malvern 2600 particle sizer was equipped with
only one standard matrix for each lens, which corresponds with one particular refractive-index ratio. Later versions of the 2600 particle sizers have been equipped with two scattering matrices per lens; one based on Fraunhofer diffraction and the other on anomalous diffraction for the case of $m \approx 1.2$. To evaluate the refractive-index ratio for which the standard matrices have been calculated, scattering matrices were computed for $m$ ranging from 1.01 to 1.5 and compared with the corresponding standard matrices. The computation of the scattering matrices is discussed in the next section. The standard matrix proved to be most similar to the matrix computed with a refractive-index ratio of $\sim 1.2$.

### III. Computation of the Scattering Matrices

For computation of the matrix coefficient $a(i, j)$ of Eq. (3), the adjacent detector elements $2i - 1$ and $2i$ were considered to consist of ten subrings and every size class of four subclasses. If $a(i, j)_{gh}$ represents the light energy scattered on subring $g$ of the detector elements $2i - 1$ and $2i$ by a unit volume fraction of subclass $h$ of size class $j$, $a(i, j)$ is given by the following summation:

$$a(i, j) = \sum_{h=1}^{10} \sum_{g=1}^{4} a(i, j)_{gh},$$

where

$$a(i, j)_{gh} = l(i, j)_{gh}/x(i)^{2}.$$  

The light energy $l(i, j)_{gh}$ is defined as the light intensity scattered by the subclass $h$ of size $x(i)$, onto subring $g$ times the area of the subring. The scattered light intensity was computed with the Mie theory. We applied the Mie subroutine as presented by Bohren and Huffman. Because the computing time for the Mie theory increases considerably with the size parameter $a(= \pi x/\lambda)^{11}$, the Mie theory was approximated with geometrical optics (GO) to reduce the computing time for large particles ($x \gg \lambda$). For large particles the incident beam of light may, in the GO approach, be considered as consisting of separate rays of light. It is possible to distinguish between the rays hitting the particle and the rays passing near the particle, giving rise to two distinct phenomena: (1) reflection and refraction, (2) Fraunhofer diffraction. We used the expressions for the GO approximation as derived by Glantschnig and Chen. To demonstrate the main features of the GO approach, we use the following approximate expression for the so-called angular intensity function:

$$i_{\text{GO}}(x, \theta, m) = 2 \cdot \alpha^{4} \cdot [J_{1}(z)]^{2} + \alpha^{2} \cdot f(m, \theta),$$

where $J_{1}(z)$ is the first-order Bessel function of the first kind and $z = \alpha \cdot \sin(\theta)$. The GO approach was used in the computation of the scattering matrices only for $\alpha > 400$, which resulted in matrix coefficients matching those computed with the Mie theory within $\sim 2\%$.

### IV. Simulation of Forward Scattering

The scattering of particles was simulated for different relative refractive indices (ranging from 1.01 to 2.0) and several size distributions (Rosin–Rammler, bimodal, etc.). The simulated scattering patterns were subsequently deconvoluted using the standard matrix, and the computed particle size distributions were compared with the original ones.

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**Fig. 2.** Fraunhofer intensity distribution.  

**Fig. 3.** Refraction function $f(m, \theta)$ versus scattering angle.
Table II. Volume Size Distributions Used in the Simulation of Forward Scattering

<table>
<thead>
<tr>
<th>No.</th>
<th>Type</th>
<th>$\bar{X}$ (μm)</th>
<th>$N$ (μm)</th>
<th>VMD (μm)</th>
<th>SMD (μm)</th>
<th>FL (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rosin–Rammler</td>
<td>10.0</td>
<td>4</td>
<td>9.17</td>
<td>8.16</td>
<td>63,500</td>
</tr>
<tr>
<td>2</td>
<td>Rosin–Rammler</td>
<td>10.0</td>
<td>2.5</td>
<td>8.98</td>
<td>6.71</td>
<td>63,500</td>
</tr>
<tr>
<td>3</td>
<td>Rosin–Rammler</td>
<td>200.0</td>
<td>3.5</td>
<td>192.68</td>
<td>159.46</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>Rosin–Rammler</td>
<td>200.0</td>
<td>2.2</td>
<td>194.76</td>
<td>124.99</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>Rosin–Rammler</td>
<td>35.0</td>
<td>4.0</td>
<td>32.06</td>
<td>28.53</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>Rosin–Rammler FL/8.57</td>
<td>2.5</td>
<td></td>
<td>FL/9.56</td>
<td>FL/12.8</td>
<td>63-1000</td>
</tr>
<tr>
<td>7</td>
<td>Broad</td>
<td>—</td>
<td>—</td>
<td>FL/12.9</td>
<td>FL/21.2</td>
<td>63,300</td>
</tr>
<tr>
<td>8</td>
<td>Broad</td>
<td>—</td>
<td>—</td>
<td>FL/7.27</td>
<td>FL/20.4</td>
<td>63,300</td>
</tr>
<tr>
<td>9</td>
<td>Bimodal</td>
<td>—</td>
<td>—</td>
<td>FL/5.56</td>
<td>FL/16.1</td>
<td>63,300</td>
</tr>
<tr>
<td>10</td>
<td>Bimodal</td>
<td>—</td>
<td>—</td>
<td>FL/7.81</td>
<td>FL/14.9</td>
<td>63,300</td>
</tr>
<tr>
<td>11</td>
<td>Bimodal</td>
<td>—</td>
<td>—</td>
<td>FL/7.27</td>
<td>FL/20.4</td>
<td>63,300</td>
</tr>
<tr>
<td>12</td>
<td>Rosin–Rammler</td>
<td>5.0</td>
<td>5</td>
<td>4.64</td>
<td>4.29</td>
<td>63</td>
</tr>
<tr>
<td>13</td>
<td>Rosin–Rammler</td>
<td>5.0</td>
<td>2.5</td>
<td>4.48</td>
<td>3.35</td>
<td>63</td>
</tr>
</tbody>
</table>

Note: In the case of a Rosin–Rammler distribution the model parameters $\bar{X}$ and $N$ are given. VMD and SMD are the volume and Sauter mean diameters, respectively, as defined by Eqs. (7) and (8). The last column lists the values of the focal length $FL$ of the lenses for which scattering patterns have been computed using the corresponding size distribution.

The various types of size distribution used in the simulation are listed in Table II. The Rosin–Rammler size distribution function is given by $Y(x) = \exp[-(x/\bar{X})^N]$, where $Y(x)$ is the volume fraction of particles with a diameter larger than $x$, $\bar{X}$ is a representative mean diameter so that 36.8% of the total particle volume is greater than $\bar{X}$, and $N$ determines the width of the distribution with $N = \infty$ for a monodisperse size distribution. The values of $\bar{X}$ and $N$ of the Rosin–Rammler distributions are given in Table II.

The broad and bimodal distributions, which are also indicated in Table II, were arbitrarily chosen and are shown in Figs. 4 and 5.

By proper choice of the lens the resolution in particle size can be optimized for the particular system of interest. Larger particles diffract light through smaller angles, and to increase the resolution in particle size a lens with a larger focal length is required to unravel the scattering at these smaller angles. As can be seen from Table II, the simulation is primarily confined to use of the 63- and 300-mm lens. For the other lenses only the errors in the deconvolution of the scattering patterns computed from distributions 6 and 7 were examined.

Figures 6 and 7 illustrate the variation in scattered light with a change in the refractive-index ratio for the 63- and 300-mm lenses, respectively. In Fig. 6 the scattering patterns for the 63-mm lens, computed with several matrices for a Rosin–Rammler distribution with $\bar{X} = 10$ μm and $N = 4.0$, are shown. The light energy patterns differ strongly after the maximum at the eighth detector element. The scattering of particles with $m = 1.20$ is most similar to the light energy pattern computed with the standard matrix. A refractive-index ratio smaller than 1.20 gives rise to an increase in the amount of light striking the outer detector elements, whereas there is a rapid decrease in light energy on the outer segments predicted by calculations with Fraunhofer diffraction. The differences in the light energy patterns on the outer segments can be explained with GO. The scattering after the maximum in the light energy distribution is mainly caused by the refraction of light by the large particles. This refraction is larger as the refractive-index ratio moves closer to 1. At smaller values of $|m - 1|$ a more intense scattering is therefore observed at the outer detector elements.

In Fig. 7 the scattering patterns for the 300-mm lens and a Rosin–Rammelr size distribution of $\bar{X} = 200$ μm and $N = 2.2$ are shown. The scattering
patterns, computed with the matrices for the 300-mm lens for several \( m \geq 1.1 \), are similar. The scattering pattern computed with \( m = 1.04 \) deviates strongly, again at the large scattering angles. The particle size of the corresponding classes increases in proportion to the focal length of the receiving lens. Because diffraction is proportional to \( x^4 \) and refraction to \( x^2 \) [Eq. (4)], the contribution of the refraction term to forward scattering becomes less important for the larger lenses. The matrices for different values of \( m \) look more similar for larger focal lengths because their major part can be adequately described with Fraunhofer diffraction, which is independent of \( m \). For \( |m - 1| \leq 0.05 \) the refraction is still appreciable, so that the light energy patterns computed for these values of \( m \) give rise to more scattering on the outer detector rings.

The computed light energy distributions were deconvoluted using the standard matrix. Deviations in the computed particle size distribution relative to the original one proved to be directly related to differences in the scattering patterns at large angles. For the 63- and 100-mm lenses the extra light energy on the outer rings for \( 1 < m < 1.2 \) can only be accounted for by larger volume fractions in the corresponding size classes, i.e., the small particles [Eq. (1)]. For \( m > 1.2 \) the opposite is true. The less scattering at large angles results in smaller volume fractions for the smaller particles, as shown in Fig. 8. For the 300-mm lens only the deconvolution of scattering patterns computed with \( m < 1.05 \) results in biased distributions. Figure 9 shows the overestimation of the volume fraction of the fine particles when the scattering pattern computed with \( m = 1.04 \) is deconvoluted with the standard matrix.

Starting from a Rosin–Rammler distribution the
fitting procedure does not return estimates for the Rosin-Rammler parameters $X$ and $N$, because it does not\textit{ a priori} assume a functional form to its solution. Instead the volume mean diameter (VMD) and the Sauter mean diameter (SMD) and a relative spread, called SPAN, are presented:

$$\text{VMD} = D_{32} = \frac{\sum n(x) \ast x}{\sum n(x) \ast x^2} = \frac{\sum q(x) \ast x}{\sum q(x) \ast x},$$  \hspace{1em} (7)

$$\text{SMD} = D_{32} = \frac{\sum n(x) \ast x^2}{\sum n(x) \ast x^3} = \frac{1}{\sum q(x)/x},$$  \hspace{1em} (8)

$$\text{SPAN} = \frac{D_{v10} - D_{v20}}{D_{v20}},$$  \hspace{1em} (9)

where $n(x)$ is the number fraction of particles of size $x$,

$q(x)$ is the volume fraction of particles of size $x$; and

$D_{v20}$ is the particle size for which the 20% volume percentage of the particles is smaller.

The VMD and SMD are related to the Rosin-Rammler parameters through the following equations:

$$\text{VMD} = X \ast \Gamma(1 + 1/N),$$  \hspace{1em} (10)

$$\text{SMD} = \frac{X}{\Gamma(1 - 1/N)},$$  \hspace{1em} (11)

where $\Gamma$ is the gamma function.

The deviations in the deconvoluted size distribution are also expressed by the values of the VMD and SMD. If the same matrix is used in the deconvolution as has been used to compute the scattering, the fitting procedure returns the values of the VMD and SMD within 5%. When the scatter patterns are deconvoluted with the standard matrix, the errors can be considerably larger. For example, Fig. 10 shows relative errors in VMD and SMD of 15 and 20%, respectively, for small values of $m - 1$ for the case of $FL = 100$ mm and distribution 6. The SMD is most affected by the inappropriate scattering matrix choice, because the value of the SMD is greatly determined by the tail of the size distribution in the small particles. In Fig. 11 the errors involved with deconvolution with the matrix based on Fraunhofer diffraction are presented, and they are even more severe than when deconvoluting with the standard matrix.

Figures 10 and 11 concern distribution 6. Figure 12 shows the relative errors in the VMD and SMD for various distributions along with the fitting error for the case of $m = 1.04$ and $FL = 300$ mm. A smaller fitting error does not imply that the resemblance between the calculated and original size distribution is better. Reduction of the fitting error depresses the random errors but not the systematic errors that are introduced into the calculated size distribution due to
the inappropriate matrix choice in the deconvolution. Figure 12 also shows that the errors seem to be slightly larger when starting from the broad and bimodal distributions.

In Table III the values of the refractive-index ratios below which the error in the SMD becomes larger than 15% are presented as a function of the focal length of the lenses. The lower limit of \( m \) where the standard matrix is still applicable in the deconvolution with errors in the SMD smaller than 15% decreases with the focal length of the lens down to \( m = 1.04 \) for the 800- and 1000-mm lenses.

It can be concluded that for a focal length of 63 and 100 mm, application of the standard matrix to systems with a refractive-index ratio ranging from 1.1 to \( m \approx 1.3 \) does not lead to significant errors in the shape of the deconvoluted volume distribution. The relative error in the VMD and SMD to be expected lies within 10 and 15%, respectively. For the larger size ranges (larger focal lengths) the application can be extended to systems with \( m \) larger than 1.3. The lower limit of application is dependent on the focal length of the Fourier-transform lens and is shown in Table III. Computation of the particle size distribution for \( m \) smaller than this lower limit is to be done preferably with the scatter matrix, which is especially calculated for the specific system.

For \( m < 1 \), the lower limit of application of the standard matrix is given by the reciprocal of the values listed in Table III.

In the case of strong absorption (absorption index \( \geq 0.01 \)) the refraction is zero. The forward-scattered intensity equals Fraunhofer diffraction. For the analysis of light scattering by strongly absorbing particles, Fraunhofer diffraction will yield the best solution to the inversion problem. Thus, for the larger lenses (> 100 mm) the standard matrix can be used. In the case of weak absorption (absorption index \( \ll 0.01 \)), the fraction of refracted light that is absorbed is a function of \( \alpha \), i.e., the size parameter. This means that for the 63- and 100-mm lenses the corresponding matrices have to be computed for all complex refractive indices. For the larger lenses only, in the case of a refractive-index ratio smaller than the values indicated in Table III, the corresponding matrix has to be calculated.

V. Experiments

For the determination of the size of ice crystals produced in a crystallization unit for the freeze concentration of sucrose solutions, two methods were used: optical microscopy and laser diffraction spectrometry.

Table III. Values of the Refractive-Index Ratio of the Particulate System Below which Deconvolution of the Scattering Patterns with the Standard Matrix may Result in Relative Errors in SMD Estimates that are Larger than 15%

<table>
<thead>
<tr>
<th>FL (mm)</th>
<th>63.0</th>
<th>100.0</th>
<th>300.0</th>
<th>600.0</th>
<th>800.0</th>
<th>1000.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>1.07</td>
<td>1.10</td>
<td>1.07</td>
<td>1.05</td>
<td>1.04</td>
<td>1.04</td>
</tr>
</tbody>
</table>

A. Optical Microscopy

Pictures of ice crystals were taken using the equipment designed by Swenne. A small slurry stream was circulated through a microscope cell. In the cell a portion of the circulated slurry can be immobilized and photographed. Figure 13 shows that some agglomeration occurred during the crystallization process. From the microscopic photographs size distributions of the agglomerates were constructed.

B. Laser Diffraction Spectrometry

The volume percentage of ice in the suspension was \( \approx 5\% \). To avoid multiple-scattering effects the ice suspension had to be diluted with mother liquor. To lower the required dilution to a factor of 2, a continuous flow cell with an optical path length of only 3 mm was constructed. In this way the melting of ice because of dilution could be limited.

The two windows in the continuous-flow cell are positioned as shown in Fig. 14 with a small angle \( \varphi \) of 0.4°. In this way the third reflection is focused just below the unreflected light beam because of inversion of the lens and does not fall onto the semicircular detector.

Warren presents a compilation of the complex refractive indices of hexagonal ice from the UV to the 2nd reflection

3rd reflection

unreflected laser beam

laser beam

Fig. 14. Relative position of windows in the continuous-flow cell.
microwave, which is valid for temperatures varying from $-60^\circ$ to $0^\circ$C. For $\lambda = 0.6328 \ \mu$m the real part of the refractive index is 1.3084, and the imaginary part is $1.1 \times 10^{-5} \approx 0$. The refractive index of the sugar solution was 1.37, giving a refractive-index ratio of $0.955$.

Because of the large size of the particles (100–500 $\mu$m) measurements with the laser diffraction apparatus were performed with an 800-mm lens. As discussed in Section IV, serious errors in the analysis using the standard matrix instead of the appropriate one are not expected for $|m - 1| \geq 0.04$ when using this large lens. Nonetheless the light scattering was processed with both matrices to determine whether this statement is correct.

C. Results

Figure 15 shows an example of the volume distributions computed with the two different matrices and the volume distribution of the agglomerates, as determined by optical microscopy. Note that the vertical and horizontal axes are presented in logarithmic form. Application of the standard matrix instead of the appropriate scattering matrix produces indeed only slightly biased results, as was expected considering the large lens that had to be used. To a first approximation the size distributions obtained with laser diffraction and microscopy are in agreement. The differences in the volume fractions of the smaller sizes originate from the following:

1) The uncertainties in the agglomerate size distribution measured by microscopy. The microscopic counting of agglomerates of the various sizes is inherently difficult and imprecise. Because $m$ was near 1, the contrast between ice crystals and the mounting medium is small, and particles smaller than 80 $\mu$m are hard to distinguish. Furthermore larger particles are always in the region of focus, and the small particles are not, resulting in an underestimation of the number of small particles present.

2) The nonspherical shape of the agglomerates. The agglomerates show the most resemblance to oblate spheroids. The aspect ratio of the agglomerates varies from 1.5 to 2.0. Because the ice crystals rise to the top of the microscopic cell and tend to direct their largest cross section toward the microscopic eye, the size distribution measured with optical microscopy corresponds merely to the largest cross sections of the agglomerates. The forward scattering of oblate spheroids can be approximated by the average scattering of an ensemble of spheres (i.e., circles), one for each projected cross section corresponding to each orientation of the spheroid. Thus the size distribution measured with laser diffraction corresponds to the projected cross-sectional area averaged over all orientations of the agglomerates. For a fair comparison with the laser diffraction result, the size distribution obtained with optical microscopy should be spread out to smaller sizes.

3) The optical inhomogeneity of the agglomerates. The agglomerates are not optically homogeneous, as assumed in the scattering theories with which the scattering matrices are computed. To take into account the inhomogeneity of the agglomerates Latimer suggested use of the average value of the refractive index of the component particles and the spaces as an estimate of the refractive index of the agglomerates. With the number of particles in the agglomerates varying from 2 to 10, the porosity of the agglomerates is $0.3$, resulting in a refractive-index ratio for the agglomerates of $0.97$. This implies that agglomerates give rise to more scattering on the outer detector rings than isotropic ice particles of the same overall size. Again this results in higher fractions of smaller particles in the analysis by laser diffraction than would be obtained in the microscopic analysis.

Considering the biasing errors mentioned in this section and the small amount of particles counted ($\sim 200$), which makes the conversion from number to volume distribution inaccurate (a relative error in volume fractions of $\sim 7\%$), the volume distribution obtained with optical microscopy agrees reasonably well with the one obtained with laser diffraction spectrometry. The determined VMD values were similar, and the SMD values differed because of the tail in the volume distribution at the small particles, which were measured by laser diffraction spectrometry but not observed by optical microscopy.

VI. Conclusions

Laser diffraction particle size analyzers that assume a fixed value of the refractive-index ratio are limited in their application to systems with other refractive-index ratios. The Malvern 2600 laser diffraction instrument referred to in Section II uses a scattering matrix corresponding to a refractive-index ratio of $\sim 1.2$. Serious errors can occur when the apparatus is used to size systems with refractive-index ratios near 1. Comparison with optical microscopy showed that laser diffraction can be a useful tool for fast on-line measurements in ice crystallization processes. Because the refractive-index ratio of these systems is near 1, it is advisable to process the measured scatter-

Fig. 15. Volume distribution of ice crystals and corresponding VMD's and SMD's determined with laser diffraction spectrometry and optical microscopy.
ing patterns with the corresponding scattering matrix instead of the standard matrix.

Appendix A: Fitting Procedure as Used in the Malvern 2600 Particle Sizer

The fitting procedure is a least-squares analysis that calculates the size distribution that gives the closest fitting scattering pattern. The fitting error is the logarithm of the least-squares error between the measured and calculated scattered-light energy data. In the fitting procedure the measured and the calculated light energy patterns are continually normalized with their peak values set to 2047. The volume size distribution is not normalized with its cumulative sum equal to 1 until it is presented as the final result of the optimization routine.

The fitting procedure makes a first guess of the size distributions using the following equation:

\[ q(i) = l(i)/a(i, i), \quad (A1) \]

where \( q(i) \) is the volume fraction of size class \( i \), \( l(i) \) is the light energy on detector rings \( 2i \) and \( 2i - 1 \), and \( a(i, i) \) is the diagonal scattering matrix coefficient.

The volume fraction of the 16th size class is extrapolated from the volume fractions of the 14th and 15th size classes:

\[ q(16) = 1.5 \times (2 \times q(15) - q(14)). \quad (A2) \]

The purpose of the initial estimate is to give the optimization routine a starting point close to the error minimum. Equation (A1) implies that the light energy \( l(i) \) scattered on the detector elements \( 2i \) and \( 2i - 1 \) is solely due to scattering by size class \( i \). This is incorrect, and before entering the final fitting routine the estimate is optimized by reducing the distribution’s width with the following iteration:

\[ q(i)^{k+1} = q(i)^{k} \times q(i)^{k}, \quad (A3) \]

where \( k \) is the iteration number.

This iteration is continued until the fitting error obtains a minimum. Next the volume distribution enters the final iteration:

\[ q(i)^{k+1} = q(i)^{k} \times \left[ \frac{l(i)_m}{l(i)_m} \right]^{1/2} + \left[ \frac{l(i + 1)_m}{l(i + 1)_m} \right]^{1/2}, \quad (A4) \]

where \( l(i)_m \) is the measured light energy on detector rings \( 2i \) and \( 2i - 1 \) and \( l(i) \) is the calculated light energy on detector rings \( 2i \) and \( 2i - 1 \).

The volume fraction of the 16th size class is multiplied with the following correction factor:

\[ q(16)^{k+1} = q(16)^{k} \times 2 \times \left[ \frac{l(16)_m}{l(16)_m} \right]^{1/2} \quad (A5) \]

where \( l(16)_m = 2 \times l(15)_m - l(14)_m \) and \( l(16)_m = 2 \times l(15)_m - l(14)_m \).

This iteration procedure requires that the light energy maxima in the matrix fall close to the diagonal. This is ensured by definition of the size classes by Eq. (1). The iteration is repeated 8 times after which the fitting error is calculated and compared with the previous one. If the fitting error is smaller than the previous one, these iterations start again. Otherwise the volume distribution that entered the last eight iteration steps will be presented as the solution to the light-scattering problem. To minimize the computing time, the iteration is also truncated if the number of iteration steps exceeds 64 and the last calculated volume distribution is presented as the solution.

References