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Multiangle dynamic light scattering analysis using a modified Chahine method

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ABSTRACT

Multiangle dynamic light scattering (MDLS) is used to determine particle size distributions (PSDs). The angular intensity weighting coefficients used in the inversion of the PSD data affect dramatically the PSD recovered. Noise in the weighting factors gives rise to poor PSD results. A modified Chahine method, which is insensitive to the noise of the weighting coefficients, is developed for estimating the PSD from MDLS. The method was evaluated through simulated examples that involved unimodal and bimodal PSDs of different shapes and employed for estimating two bimodal PSDs obtained by mixing two standard polystyrene latexes. For comparison, all examples were also analyzed using a nonnegatively-constrained Tikhonov regularization technique typically used for inverting ill-conditioned linear problems. The PSDs estimated by the proposed modified Chahine method were more accurate than those obtained by the Tikhonov technique.

1. Introduction

Dynamic light scattering (DLS) is a widely used technique for estimating the particle size distribution (PSD) of colloidal systems with particles in the submicrometer range [1–3]. It is a fast, convenient and relatively simple technique. However, this technique has limitations due to the relatively low information content inherent in the measured signal and, consequently, poor PSD resolution can be expected. Multiangle dynamic light scattering (MDLS) compensates for the low information in a single-angle correlation function by including the correlation functions of the other measurement angles, which are influenced by the different scattering characteristics and dynamics of the particles for different scattering angles. So MDLS provides more information for the estimation of the PSD.

Cummins and Staples proposed MDLS in 1987 using the nonnegative least squares technique (NNLS) to estimate the PSD from two-angle DLS [4]. Since then numerous approaches have been proposed to estimate the PSD from MDLS. These include the constrained regularization method (CONTIN) [5], the singular value decomposition (SVD) [6] and the regularization method [7,8]. More recently, intelligent-optimization-based algorithms involving the neural network approach [9] and a Bayesian inversion method [10] have been developed. However, these techniques are sensitive to noise in the angular intensity weighting coefficients, which adds noise to the PSD estimation. Errors in the weighting coefficients may seriously compromise the PSD estimation.

Bryant and Thomas used a combination of static light scattering (SLS) and MDLS to obtain more measurement information and improved PSD determination [11]. For these experiments accurate SLS measurements were made to give the angular dependence of the scattered

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light, which was then used to weight each DLS angle in the MDLS analysis. This requires a high quality optical goniometer system capable of precision SLS measurements and increases significantly the measurement time. Subsequently, Bryant et al. [12] demonstrated that similarly improved PSD results could be obtained from MDLS using an iterative technique to reconstruct the SLS. Vega [13] proposed a recursive least-squares method to estimate the weighting coefficients using the complete autocorrelation function measurement. The recursive method proposed by Vega and the iterative technique proposed by Bryant et al. rely on a good estimate of the PSD at each step. This, in turn, relies on the choice of regularization parameter.

The Chahine method used in this work uses the weighting coefficients calculated from the baselines of the autocorrelation functions and gives good estimates of the PSD despite the noise in the weighting coefficients. The Chahine method does not need any parameter, which is difficult to determine. The method is simple and robust compared with the MDLS inversion methods proposed above.

2. The theory of MDLS and the modified Chahine inversion method

In MDLS, measurements of the intensity autocorrelation function (ACF) are taken at different values of scattering angle, θ_r. The measured intensity ACFs are related to the normalized ACFs of the electric field, $g^{(1)}_{\theta_r}(\tau_j)$ through

$$G^{(2)}_{\theta_r}(\tau_j) = G^{(2)}_{\infty,\theta_r}(1+\beta|g^{(1)}_{\theta_r}(\tau_j)|^2) \quad r=1,2,\ldots,R \text{ and } j=1,2,\ldots,M_r \tag{1}$$

where $G^{(2)}_{\theta_r}(\tau_j)$ is the autocorrelation function of the scattered light intensity, $G^{(2)}_{\infty,\theta_r}(\tau_j)$ is the measured baseline, $\beta(\leq 1)$ is an instrumental coherence parameter, R is the total number of the scattering angles, and M_r is the total number of correlator channels or points of the autocorrelation function measured at θ_r. If the PSD is described by a number distribution $f(D_i)$ of particle sizes, D_i, then at a given angle, $g^{(1)}_{\theta_r}(\tau_j)$ is related to the PSD by [13]

$$g^{(1)}_{\theta_r}(\tau_j) = k_{\theta_r}\sum_{i=1}^{N}\exp[-\Gamma_0(\theta_r)\tau_j/D_i]C_{I,\theta_r}(D_i)f(D_i) \tag{2}$$

with

$$\Gamma_0(\theta_r) = \frac{16\pi k_B T}{3\eta}\left(\frac{n_m(\lambda)}{\lambda_0}\right)^2\sin^2\left(\frac{\theta_r}{2}\right). \tag{3}$$

here k_{θ_r} are *a priori* unknown proportionality constants or weighting coefficients. $C_{I,\theta_r}(D_i)$ is the fraction of light intensity scattered by a particle of diameter D_i at θ_r and is calculated through the Mie scattering theory [14]. k_B is the Boltzmann constant, T is the absolute temperature, η is the medium viscosity at T, $n_m(\lambda)$ is the refractive index of the non-absorbing suspending liquid and λ_0 is the *in-vacuo* wavelength of the incident laser light.

In vector notation, Eq. (2) can be written as $\mathbf{g}^{(1)}_{\theta_r} = k_{\theta_r}\mathbf{H}_{\theta_r}\mathbf{f}$, where $\mathbf{g}^{(1)}_{\theta_r}$ is the vector with elements of $g^{(1)}_{\theta_r}(\tau_j)$, $\mathbf{H}_{\theta_r}$ is the matrix including elements of $\exp[-\Gamma_0(\theta_r)\tau_j/D_i]C_{I,\theta_r}(D_i)$ and $\mathbf{f}$ is the vector containing elements of $f(D_i)$.

A dimensionless weighting ratio, $k^*_{\theta_r}$, relative to a fixed reference angle θ_1 can be defined as,

$$k^*_{\theta_r} = \frac{k_{\theta_r}}{k_{\theta_1}} = \left[\frac{G^{(2)}_{\infty,\theta_1}}{G^{(2)}_{\infty,\theta_r}}\right]^{1/2} = \frac{\langle I_{\theta_1}\rangle}{\langle I_{\theta_r}\rangle} \tag{4}$$

Eq.(4) suggests the weighting ratios $k^*_{\theta_r}$ can be determined from the autocorrelation baselines $G^{(2)}_{\infty,\theta_1}$ and $G^{(2)}_{\infty,\theta_r}$. However, the method proposed above relies on the experimental measurements, which may contain sufficient noise to corrupt the estimates of the weighting coefficients. In this work the Chahine method, which is relatively insensitive to the noise of the weighting coefficients, is used for estimating the PSD to improve the inversion precision.

The Chahine method was originally proposed for measuring the distribution of atmospheric temperature, and it was not used for particle measurement until 1971 [15]. Extinction [16], forward light scattering [17] and transmission fluctuation spectrometry [18] have been used to estimate the PSD of micron-sized particles using the Chahine method. The modified Twomey-Chahine method was proposed in 1975 [19] as the original Chahine method is affected by a number of factors, such as measurement errors, which lead to oscillations in the results. However, the Twomey-Chahine method requires a smooth matrix [20] and initial iteration values close to the true values [21]. These limitations led to other modified Chahine methods being proposed [22,23].

In the initial Chahine method, the modified formula for the distribution function is

$$f^{(p)}_i = \frac{g_{meas}}{g^{(p-1)}_{calc}}f^{(p-1)}_i \tag{5}$$

where $f^{(p)}_i$ is the component of the PSD due to the discrete diameter D_i after the p^{th} iteration. The modifying factor is $C^{(p)} = g_{meas}/g^{(p-1)}_{calc}$, where g_{meas} is the measured autocorrelation function data and $g^{(p-1)}_{calc}$ is the calculated autocorrelation function data from the $(p-1)^{\text{th}}$ iteration,

$$g^{(p-1)}_{calc,n} = \sum_{i=1}^{K} h_{n,i}f^{(p-1)}_i \tag{6}$$

where $g^{(p-1)}_{calc,n}$ are the elements of the vector $\mathbf{g}^{(p-1)}_{calc}$, $h_{n,i}$ are the elements of the matrix $\mathbf{H}_{\theta_r}$.

Here it is required that the number of particle size intervals equals the number of calculated values to ensure the stability of the inversion results [24]. When the relationship is not satisfied, the result is unstable. Ferri et al. [16] proposed a new iterative form of Eq. (5) to improve the particle sizing accuracy of the spectral extinction data,

$$f^{(p)}_i = f^{(p-1)}_i \cdot \sum_{n=1}^{M} u_{n,i}\frac{g_{meas,n}}{g^{(p-1)}_{calc,n}} \tag{7}$$

where $u_{n,i} = h_{n,i}/\sum_{i=1}^{N} h_{n,i}$ are the elements of the matrix $\mathbf{U}$, $g_{meas,n}$ are the elements of the vector $\mathbf{g}_{meas}$, $g^{(p-1)}_{calc,n}$ are the elements of the vector $\mathbf{g}^{(p-1)}_{calc}$. However, the values of the measured intensity ACF ($g_{meas,n}$) in MDLS depend more weakly on particle size than does extinction data. The PSD estimate will be unstable if eq. (7) is used for MDLS analysis. In order to make the PSD estimate much more stable and reliable, a modified form of Eq. (7) is used in this work for the inversion of the MDLS data as follows,

$$f_i^{(p)} = f_i^{(p-1)} \cdot \frac{\sum_{n=1}^{M} u_{n,i} g_{meas,n}}{\sum_{n=1}^{M} u_{n,i} g_{calc,n}^{(p-1)}} \tag{8}$$

In this work, the modified Chahine method is used for estimating the PSD of the nanoparticles from MDLS data. The modified Chahine method used in this work is relatively insensitive to the initial iteration values and avoids the problem of poor initial iteration values biasing the PSD estimate away from the true value. Of course the number of iterations may increase when the initial iteration guesses are far away from the true values. The procedure for implementing the modified Chahine method used in this work is as follows:

(1) Calculate the PSD estimate obtained at the reference angle (30°) and set as the initial iterative values $f^{(0)}$.
(2) Calculate the matrix $\mathbf{U}$ containing elements $u_{n,i} = h_{n,i} / \sum_{i=1}^{N} h_{n,i}$ using $h_{n,i}$, the elements of the matrix $\mathbf{H}_{\theta_r}$.
(3) Update the iterative values $f_i^{(p)} = f_i^{(p-1)} \cdot \frac{\sum_{n=1}^{M} u_{n,i} g_{meas,n}}{\sum_{n-1}^{M} u_{n,i} g_{calc,n}^{(p-1)}}$.
(4) Calculate the root-mean-squared-error (RMSE) between $g_{calc,i}^{(p)}$ and $g_{meas,i}$: $RESM^{(p)} = \left\{ \frac{1}{M} \sum_{n=1}^{M} (g_{meas,n} - g_{calc,n}^{(p)})^2 \right\}^{1/2}$ and, when this satisfies $\left| 1 - \frac{RMSE^{(p)}}{RMSE^{(p-1)}} \right| \le 1 \times 10^{-5}$, stop the iteration and make $f = f^{(p)}$.

3. Validation of the proposed method

Simulated example data were constructed for validating the proposed estimation method. The data were simulated for a constant temperature $T = 298.15$ K, solution viscosity $\eta = 0.89$ mPas and a vertically-polarized HeNe laser of wavelength $\lambda_0 = 632.8$ nm. At this λ, the particle refractive index is $n_p = 1.57$ and suspending liquid refractive index is $n_m = 1.33$. The measurement angles were selected at 20° intervals in the range 30° to 130°. The baseline values were calculated from

$$G_{\infty,\theta_r}^{(2)} = c \left[\sum_{i=1}^{N} C_{I,\theta_r}(D_i) f(D_i) \right]^2 \quad \theta_r = \theta_1, \theta_2, \ldots, \theta_R \tag{9}$$

where $c = 10^{-6}$ and the 'true' weighting coefficients were calculated through the second equality of Eq.(4) from the baselines and the reference angle. The quality of the PSD estimate was determined by comparing the true (simulated) PSD and estimated PSD size-by-size. This was used to compute a performance index V as follows;

$$V = \left\{ \sum_{i=1}^{K} \left[f(D_i) - f(\hat{D}_i) \right]^2 \right\}^{1/2}$$

where $f(D_i)$ is the 'true' PSD and $f(\hat{D}_i)$ is the PSD estimate and K is the number of particle sizes in the distribution.

The unimodal PSD, was a log-normal [13]

$$F(D_i) = \frac{N_p}{D_i \sigma \sqrt{2\pi}} \exp\left[-\frac{[\ln(D_i/D_g)]^2}{2\sigma^2} \right]$$

and the bimodal PSD was defined by combining two log-normal distributions as follows,

$$F(D_i) = 0.75 \frac{N_p}{D_i \sigma_1 \sqrt{2\pi}} \exp\left[-\frac{[\ln(D_i/D_{g,1})]^2}{2\sigma_1^2} \right] + 0.25 \frac{N_p}{D_i \sigma_2 \sqrt{2\pi}} \exp\left[-\frac{[\ln(D_i/D_{g,2})]^2}{2\sigma_2^1} \right]$$

here N_p is the particle number concentration, D_i is the discrete diameter, D_g, $D_{g,1}$ and $D_{g,2}$ are the geometric mean diameters and σ, σ_1 and σ_2 are the geometric mean standard deviations (the standard deviations of $\ln(D_i)$), respectively [25]. The standard deviations, the simulated size ranges and intervals and the estimated size ranges and intervals are as shown in Table 1.

For these examples, the simulated intensity ACF values were used as the measured values and inverted to determine the PSD. The Tikhonov technique with automatic selection of the regularization parameters using the L-curve method [26] and the generalized cross-validation (GCV) criteria [27], and the modified Chahine method were used to invert the data.

Fig. 1a, b and c show the inversion results from the three unimodal data sets and Table 2 shows the 'true' and the estimated PSD parameters, the relative errors between the two and the performance index values.

Table 1
Parameters used to simulate and analyze log normal particle size distributions.

	Geometric mean standard deviation	Size range for simulation (nm)	Number of points for simulation	Size range for analysis (nm)	Number of points for analysis
Wide unimodal distribution at 590 nm	0.15	200–1000	160	100–1100	60
Narrow unimodal distribution at 500 nm	0.075	150–850	140	100–1000	90
Unimodal distribution at 200 nm	0.1	80–320	80	20–400	50
Bimodal distribution at 500 nm and 800 nm	0.13/0.045	30–1000	140	200–1100	100
Bimodal distribution at 300 nm and 700 nm	0.13/0.045	150–850	140	50–1000	125

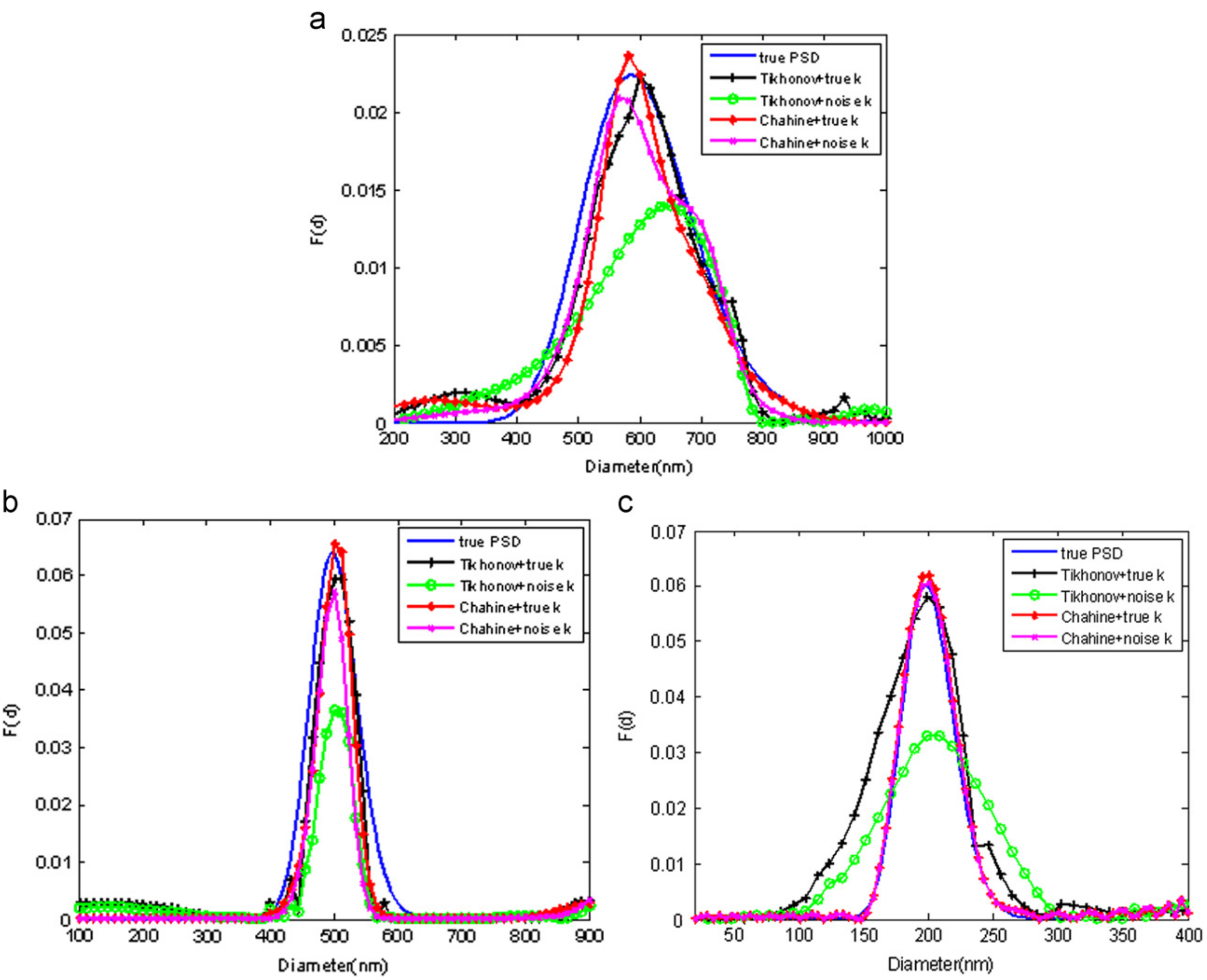

Fig. 1. (a) Simulated and estimated values for a 590 nm unimodal particle size distribution. (b) Simulated and estimated values for a 500 nm unimodal particle size distribution. (c) Simulated and estimated values for a 200 nm unimodal particle size distribution.

Table 2
'True' and estimated particle size distributions, relative errors and performance index values (V) for the simulated unimodal size distributions.

	True Value (f)	Tikhonov+true k (f_1)	Chahine+true k (f_2)	Tikhonov+noise k (f_3)	Chahine+noise k (f_4)
Diameter(a)/nm	590	600	584	650	580
Relative error(a)/%		1.69	1.02	10.17	1.69
V		0.012	0.011	0.029	0.013
Diameter(b)/nm	500	500	500	510	500
Relative error(b)/%		0	0	2.00	0
V		0.042	0.041	0.086	0.046
Diameter(c)/nm	200	200	200	208	200
Relative error(c)/%		0	0	4.00	0
V		0.053	0.014	0.057	0.011

Relative error$=(|f-f_i|/f)\times 100\%$ ($i=1,2,3,4$), respectively.

Likewise, Fig. 2a and b and Table 3 show the corresponding results for the bimodal distributions. In the figures and tables, 'Tikhonov+true k', 'Tikhonov+noise k', 'Chahine+true k' and 'Chahine+noise k', respectively represent the PSD estimates obtained by Tikhonov technique using the 'true' weighting ratios and using the 'true' weighting ratios with added noise, the modified Chahine technique using the 'true' weighting ratios and using the 'true' weighting ratios with added noise. Added noise means that random noise with an error band of $\pm 1\%$ was added to the angular intensity weighting coefficients.

For the unimodal distribution with 'true' weighting ratios the recovered PSDs from both the Tikhonov and the modified Chahine methods match the real PSDs well

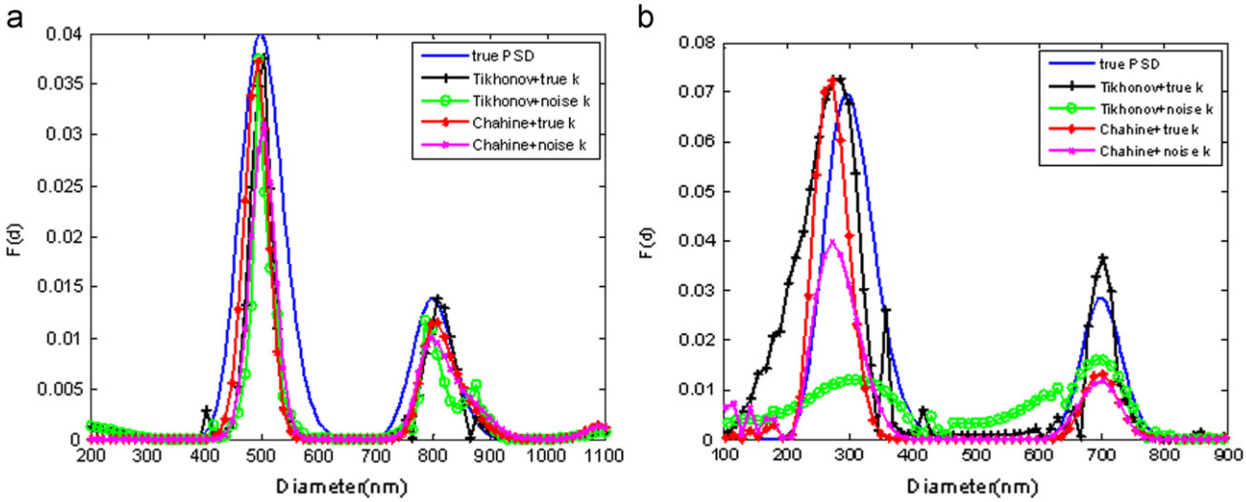

Fig. 2. (a) Simulated and estimated values for a bimodal particle size distribution with peaks at 500 nm and 800 nm. (b) Simulated and estimated values for a bimodal particle size distribution with peaks at 300 nm and 700 nm.

Table 3
'True' and estimated particle size distributions, relative errors and performance index values (V) for simulated bimodal size distributions.

	True Value (f)	Tikhonov+true k (f_1)	Chahine+true k (f_2)	Tikhonov+noise k (f_3)	Chahine+noise k (f_4)
Diameter(a)/nm	500/800	503/806	495/806	495/785	503/797
Relative error(a)/%		0.60/0.75	1.00/0.75	1.00/0.50	0.60/0.38
V		0.033	0.033	0.060	0.036
Diameter(b)/nm	300/700	290/702	280/701	297/701	280/701
Relative error(b)/%		3.33/0.29	6.67/0.14	1.00/0.14	6.67/0.14
V		0.108	0.102	0.136	0.110

Relative error$=(|f-f_i|/f)\times 100\%$ ($i=1,2,3,4$), respectively.

regardless of whether there is a wide or narrow unimodal distribution, as shown in Fig. 1a, b and c. However, the Chahine method gave a slightly smaller relative error and better performance index values and the PSDs were smoother and more narrow. For the bimodal distribution with large particles (500 nm and 800 nm) it can be seen in Fig. 2a that, even if the peak position ratio is less than 1:2, both the Chahine and the Tikhonov methods give good estimates of the PSD. However, for the bimodal distribution at small particle size (300 nm and 700 nm), the modified Chahine method has no obvious advantages compared with the Tikhonov technique and underestimates the small peak position by ~7%, as shown in Fig. 2b and Table 3. The reasons for the large relative error will be discussed later in the text.

When 1% noise is added to the weighting ratios it can be seen that, for all the unimodal distributions and the bimodal distribution at large size, the Chahine method gives a better inversion result than the Tikhonov technique. However, for the bimodal distribution with the small particle peak at 300 nm, the modified Chahine method again places that peak at 280 nm, which is ~7% low.

It can be seen that for all the simulated examples, the Chahine method gave almost the same PSD estimations with the 'true' weighting ratios and the weighting ratios with noise indicating that the noise of the weighting ratios has little effect on the resulting PSD. However, for the Tikhonov technique, the weighting ratios with noise have a large effect on the PSD estimate.

To investigate further the performance of the modified Chahine method with noisy angular weights the unimodal distributions at 200 nm and 590 nm and the bimodal distribution with the 500 nm and 800 nm components were re-analyzed using angular weighting coefficients with increasing amounts of noise added. Noise was added at the level of ±1%, ±2%, ±5% and ±10%. The inversion results are shown in Fig. 3a, b and c where the labels indicate the amount of added noise. Table 4 shows the parameters for the 'true' and estimated PSDs, the relative errors between them and the performance index values for the different levels of noise on the weighting coefficients.'For the unimodal distributions the modified Chahine method gave good peak values of 200 nm and 584 nm, respectively for all noise levels. This can be seen in Fig. 3a and b and Table 4. However, the peak heights decrease as the noise increases. The poor peak heights give rise to the increased (poorer) performance index values shown in Table 4.

For the bimodal distribution of 500 nm and 800 nm, there is little difference between the PSD estimates at the different noise levels, as can be seen in Fig. 3c, even though the relative errors and the performance index

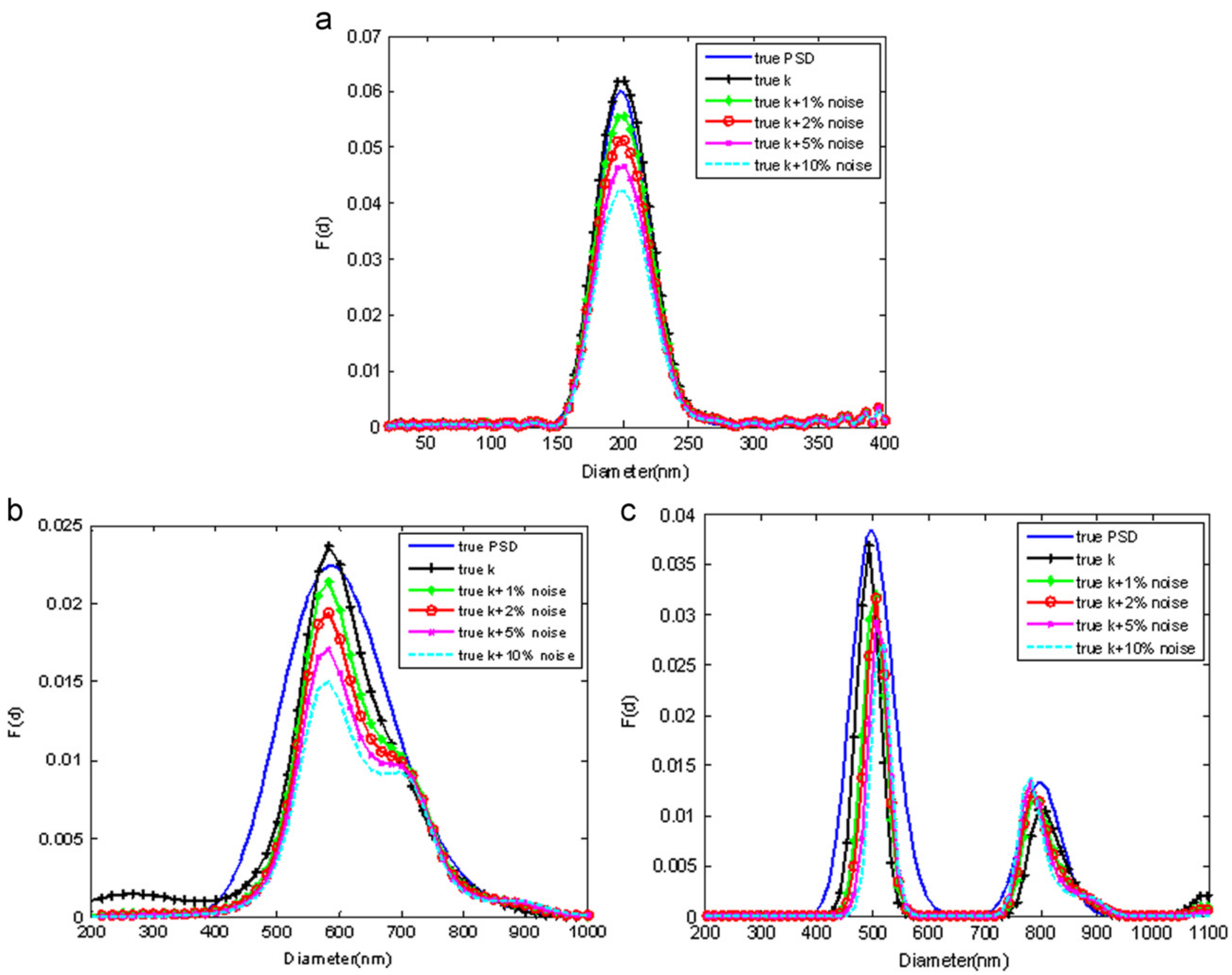

Fig. 3. (a) Simulated and estimated values for a 200 nm unimodal particle size distribution. Data analysis performed with angular weighting coefficients containing different levels of noise. (b) Simulated and estimated values for a 590 nm unimodal particle size distribution. Data analysis performed with angular weighting coefficients containing different levels of noise. (c) Simulated and estimated values for a bimodal particle size distribution with peaks at 500 nm and 800 nm. Data analysis performed with angular weighting coefficients containing different levels of noise.

Table 4
'True' and estimated particle size distributions, relative errors and performance index values (V) for simulated examples using angular weighting coefficients with different noise levels.

	True Value (f)	true k (f_1)	true k+1% noise (f_2)	true k+2% noise (f_3)	true k+5% noise (f_4)	true k+10% noise (f_5)
Diameter(a)/nm	200	200	200	200	200	200
Relative error(a)/%		0	0	0	0	0
V		0.014	0.015	0.021	0.034	0.046
Diameter(a)/nm	590	584	584	584	584	584
Relative error(a)/%		1.02	1.02	1.02	1.02	1.02
V		0.016	0.021	0.023	0.027	0.031
Diameter(a)/nm	500/800	495/797	505/795	505/792	505/789	507/789
Relative error(a)/%		1.00/0.38	1.00/0.63	1.00/1.00	1.00/1.38	1.40/1.38
V		0.040	0.045	0.048	0.054	0.059

Relative error$=(|f-f_i|/f)\times 100\%$ (i=1,2,3,4,5), respectively.

values increased slightly with added noise level as shown in Table 4. It appears that the presence of noise on the weighting coefficients has little effect on the PSD determination by the modified Chahine method for a bimodal distribution.

4. Application to experimental data

A schematic diagram and photograph of the experimental instrument are shown in Fig. 4. It consists of a vertically-polarized HeNe laser (wavelength 632.8 nm)

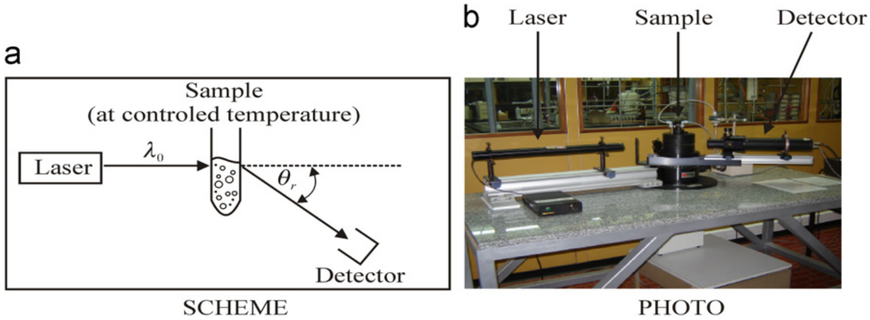

Fig. 4. Schematic diagram and photograph of the experimental apparatus.

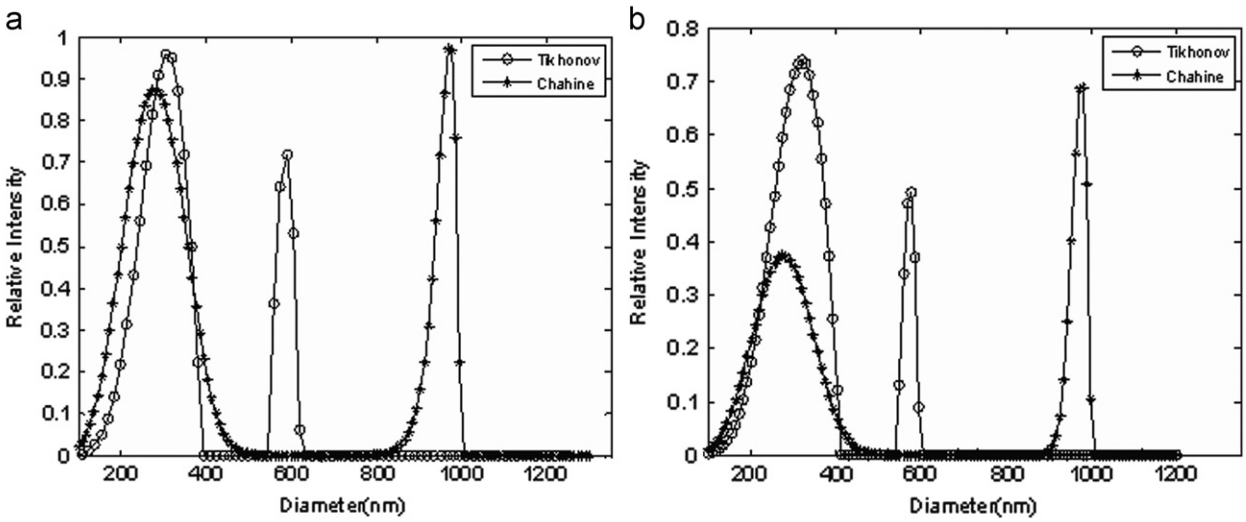

Fig. 5. (a) Estimated particle size distribution for a 306 nm and 974 nm bimodal latex sphere sample mixed in the ratio 1:1. (b) The estimated particle size distribution for a 306 nm and 974 nm bimodal latex sphere sample mixed in the ratio 1:2.

and a photomultiplier tube as a detector. The sample is in a temperature controlled bath at 298.15 K. A hardware-based digital autocorrelator (model BI-2000 AT) allowed automatic acquisition of the second-order ACF $G_{\theta_r}^{(2)}(\tau_j)$, at several scattering angles θ_r. Prior to carrying out the measurements, the equipment was properly checked for angular alignment. The MDLS was carried out in the detection angle range 30° to 130° at intervals of 20°.

The samples used to collect experimental data were two bimodal mixtures made up of standard polystyrene latices with nominal diameters of 306 nm and 974 nm. For the first bimodal sample, the intensity ratio was approximately 1:1, and for the second, the intensity ratio was approximately 1:2.

The weighting ratios $k_{\theta_r}^*$ were calculated through the second equality of Eq. (4) from the baselines and the reference scattering angle. Then the matrix $\mathbf{H}_{\theta_r}$ was calculated and the data were inverted to recover the PSD using the Tikhonov technique with automatic selection of the regularization parameters using the L-curve method and the modified Chahine method. The inversion results are shown in Fig. 5a and b. The intensity ACFs of the two bimodal distributions are shown in Fig. 6. Table 5 shows the 'true' particle sizes, the estimated particle sizes, the relative errors between them and the peak height ratios.

As shown in Fig. 5, the PSD estimates obtained through the modified Chahine method are more accurate than the PSD estimates obtained through the Tikhonov technique. Furthermore, the PSDs estimated through the Tikhonov technique look suspect. This is because the weighting ratios estimated using the experimental baselines with a lot of noise, as shown in Fig. 6, are imprecise and the weighting ratios with a lot of noise corrupt the PSD estimation seriously for the common inversion methods, such as the Tikhonov technique. However, the modified Chahine method is hardly affected by the experimental baselines, which have a lot of noise. The modified Chahine method gave good inversion results using the weighting ratios estimated through the experimental baselines, even through the experimental baselines have a lot of noise.

5. Discussion of the inversion results

The inversion results from the simulated data showed that the modified Chahine method gave good PSD estimates for the unimodal distributions for both wide and narrow PSDs. Good results were also obtained for the

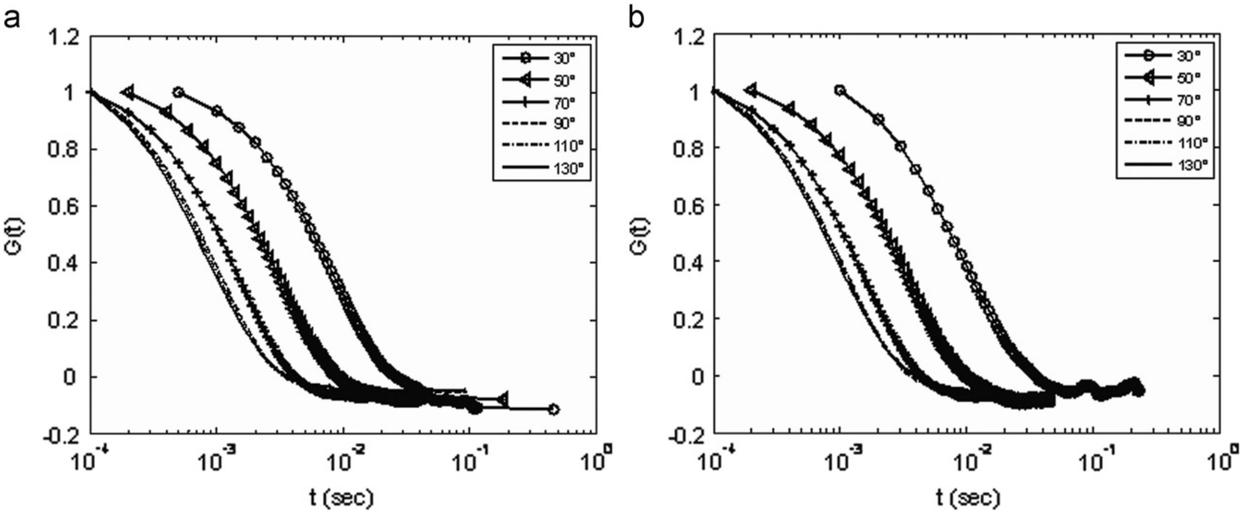

Fig. 6. Intensity autocorrelation function for the first (a) and the second (b) experimental bimodal distribution of polystyrene latex spheres.

Table 5
'True' and estimated particle sizes, relative errors and peak height ratios for the experimental bimodal particle size distribution.

	True Values (f)	Tikhonov (f_1)	Chahine (f_2)
Diameter(a)/nm	306/974	305/593	287/976
Relative error(a)/%		0.33/39.12	6.21/0.21
Peak height ratios(a)	1:1	1.4:1	1:1.1
Diameter(b)/nm	306/974	320/577	284/971
Relative error(b)/%		4.58/40.76	7.19/0.31
Peak height ratios (b)	1:2	1.5:1	1:1.9

Relative error$=(|f-f_i|/f)\times 100\%$ ($i=1,2$), respectively.

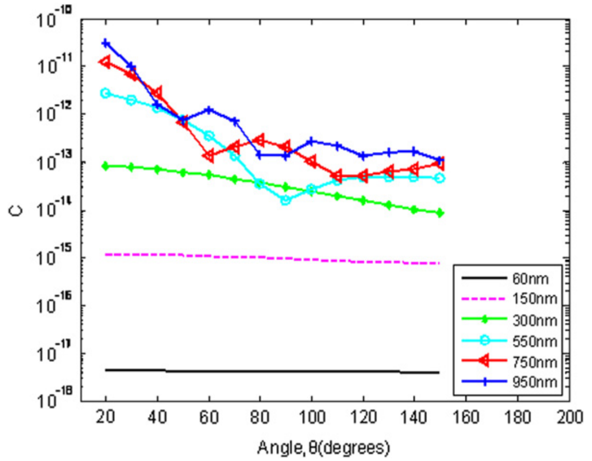

Fig. 7. Mie scattering coefficients of polystyrene latex spheres suspended in water and for a laser wavelength of 632.8 nm for a range of particle diameters.

bimodal distribution of 500 nm and 800 nm. However, for the bimodal distribution consisting of 300 nm and 700 nm particles, the small particle peak at 300 nm was not recovered well.

The experimental data inversion results showed that the modified Chahine method gives good results for the particles of 974 nm, but underestimated the nominal 306 nm peak by ~6%, which is a small error. This small error is not significant and may arise because MDLS relies on the different angular scattering properties of the particles to provide additional information. For large particles, the light scattered by a particle depends strongly on the scattering angles and a set of measurements taken at several scattering angles would be able to capture more information on particle size than a single measurement at a given scattering angle. However, for small particles there is a less pronounced variation of scattering intensity with angle, so the MDLS measurements would incorporate less additional information on the particle sizes for small particles. This is illustrated in Fig. 7, which shows the Mie scattering coefficients as a function of scattering angle for a range of diameters D_i.

It can be seen from Fig. 7 that, for particle sizes larger than ~150 nm, the light scattering has obvious variation at different scattering angles, and the larger the particle size, the more pronounced the variation. For particle sizes in the range ~60–150 nm, the light scattering has less pronounced variation with scattering angle, and for particle sizes smaller than ~60 nm, the particles scatters almost the same amount of light at all scattering angles according to the Rayleigh scattering model. The modifying factor of the Chahine method used in this work is based on the angular variation of the scattered light. In a bimodal distribution, the light scattering from small particles has little angular variation relative to the large particles. So the modified Chahine method is less sensitive to the variation of light scattering from the small particles in a bimodal distribution and is less able to accurately resolve the small (300 nm) particles in the simulated bimodal distribution of 300 nm and 700 nm particles or the small (306 nm) particles in the experimental bimodal distribution of 306 nm and 974 nm particles.

6. Conclusions

An inversion technique based on a modified Chahine method is used for estimating the PSD from MDLS measurements. This method is relatively insensitive to the noise on the angular intensity weighting coefficients. The method was successfully demonstrated using simulated and experimental examples. The inversion results have shown that the method gives good estimates of the PSD for unimodal distributions and large particles in bimodal distributions while it underestimates the small size peak positions in a bimodal distribution by $\sim$7%. This may be due to the relationship between the angular light scattering and the particle sizes. The modified Chahine method gives better experimental PSD estimates than the Tikhonov technique using weighting ratios obtained by the ACF baselines, especially when there is noise on the weighting coefficients. For unimodal distributions, the modified Chahine method using the angular weighting coefficients with different noise gave good peak values and, for bimodal distributions, the modified Chahine method results were relatively unaffected by large amounts of noise (up to 10%) on the weighting coefficients. These results indicate that method proposed is robust and has advantages over other methods commonly used in recovering PSD information from MDLS measurements.

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