CRAMÉR-RAO BOUNDS FOR PARTICLE SIZE DISTRIBUTION ESTIMATION FROM MULTIANGLE DYNAMIC LIGHT SCATTERING

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ABSTRACT

We derive the Cramér-Rao lower bounds (CRB) for parametric estimation of the number-weighted particle size distribution (PSD) from multiangle Dynamic Light Scattering (DLS) measurements. The CRB is a useful statistical tool to investigate the optimality of the PSD estimators. In the present paper, a Gaussian mixture (GM) model of the multimodal PSD is assumed and the associated Fisher information matrix (FIM) is determined. The usefulness of multiangle DLS in significantly decreasing the CRB is demonstrated. The mean square error (MSE) of the PSD GM model parameters estimation by the Bayesian inference method proposed in [1] is compared to the derived CRB for a simulated monomodal PSD. Results show that the MSE achieves the derived CRBs for the unbiased estimators of the PSD GM model parameters.

***Index Terms*—** Particle Size Distribution, Multiangle Dynamic Light Scattering, Cramér-Rao Bound, Inverse Problem, Bayesian Inference.

1. INTRODUCTION

Dynamic light Scattering (DLS) is a standard technique frequently used for measuring the size distribution of submicrometric particles dispersed in a dilute dispersion [2]. The main advantages of this technique compared to other techniques in the same size range come from the fact that it is non-invasive, fast, and provides an absolute estimate of particle size. The DLS technique is based on the analysis of the temporal fluctuations of light scattered by the illuminated particles at a given angle. These fluctuations are due to the random Brownian motion of the dispersed particles [2, 3].

DLS involves the analysis of the time autocorrelation function (ACF) of light intensity scattered at an angle θ. This time ACF is performed by a digital correlator. The measured normalized intensity time ACF, $\mathrm{g}_\theta^{(2)}(\tau)$, may be expressed in terms of the normalized electric field time ACF, $\mathrm{g}_\theta^{(1)}(\tau)$, as [3]

$$\mathrm{g}_\theta^{(2)}(\tau) = 1 + \beta|\mathrm{g}_\theta^{(1)}(\tau)|^2, \tag{1}$$

where τ is the time delay and $\beta(< 1)$ is an instrumental factor.

For a polydisperse sample of non-interacting spherical particles, the electric field time ACF, $\mathrm{g}_\theta^{(1)}(\tau)$, is related to the number-weighted particle size distribution (PSD), $f(D)$, by [4]

$$\mathrm{g}_\theta^{(1)}(\tau) = \frac{1}{k_\theta}\int_0^\infty f(D)C_I(\theta, D)\exp(-\frac{\Gamma_0(\theta)}{D}\tau)\mathrm{d}D, \tag{2}$$

where D is the hydrodynamic diameter and $C_I(\theta, D)$ is the number to intensity conversion factor (Mie theory [5]). $\Gamma_0(\theta) = \frac{16\pi n^2\sin^2(\theta/2)k_B\mathrm{T}}{3\lambda_0^2\eta}$ with k_B, T and λ_0 are the Boltzmann constant, the absolute temperature and the wavelength of laser light in vacuum, respectively. n is the medium refractive index and η is the viscosity. $k_\theta = \int_0^\infty f(D)C_I(\theta, D)\mathrm{d}D$ is a weighting coefficient.

Estimating the PSD from DLS measurements involves the inversion of the integral equation (2). This problem is known to be an ill-conditioned inverse problem which may possess no unique solution. Many different methods have been proposed to estimate the PSD from single-angle DLS data [6–10]. The commonly used are the cumulants method [6] and CONTIN [7]. These methods work well for monomodal PSD. However, their robustness and reproducibility are not good [2] and their capacity to discriminate peaks of multimodal PSDs is poor especially when the peaks ratio is less than 2.

Multiangle DLS (MDLS), which consists in analysing simultaneously the DLS data acquired at different angles, allows to get more information about the sample. MDLS significantly improves the resolution, robustness and reproducibility of the PSD estimation [4, 11–13].

In [1], we proposed a Bayesian inference based method for the estimation of multimodal PSDs from MDLS measurements. The PSD is modelled as a Gaussian mixture (GM) with an unknown number of modes. The derived *posterior* probability distribution of the unknown GM model parameters is sampled using a reversible jump Markov chain Monte Carlo (RJMCMC) algorithm [14]. The method is able to separate the PSD modes even if their ratio is less than 2.

In the present paper, we aim at assessing the robustness of the proposed method [1]. To this end, we derive the Cramér-Rao Bound (CRB) expressions for parameter estimates of

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the PSD GM model. The CRBs represent the lower bounds that the mean square error (MSE) of unbiased estimators can achieve. To our knowledge, no previous works have derived the CRB expression for the PSD estimation in DLS. First, we demonstrate the usefulness of multiangle DLS in decreasing the CRBs. Then, the robustness of the proposed method [1] is evaluated by comparing the MSE with the derived CRBs.

The paper is organized as follow. Section 2 gives a brief description of the inversion method proposed in [1]. Section 3 details the derivation of the Fisher information matrix (FIM) expressions and therefore those of the CRBs, from the log-likelihood function. Results obtained from simulated data and comparison of the MSE with the CRB are presented in section 4. Finally, conclusions are drawn in section 5.

2. PROPOSED BAYESIAN INVERSION METHOD

The proposed method in [1] is a multiangle DLS analysis. The DLS measurements are acquired at different scattering angles $\{\theta_r, r = 1, \ldots, R\}$ with R is the total number of scattering angles. For each angle θ_r, the intensity time ACF $\mathrm{g}^{(2)}_{\theta_r}(\tau)$ is measured at discrete time delays $\{\tau_m, m = 1, \ldots, M_r\}$ with M_r is the total number of points.

An additive noise model is proposed to model the measured intensity time ACFs, $\tilde{\mathrm{g}}^{(2)}_{\theta_r}(\tau_m)$, as follow

$$\begin{aligned} \tilde{\mathrm{g}}^{(2)}_{\theta_1}(\tau_m) &= \mathrm{g}^{(2)}_{\theta_1}(\tau_m) + n_1(m), \quad m = 1, \cdots, M_1 \;, \\ &\vdots \\ \tilde{\mathrm{g}}^{(2)}_{\theta_r}(\tau_m) &= \mathrm{g}^{(2)}_{\theta_r}(\tau_m) + n_r(m), \quad m = 1, \cdots, M_r \;, \\ &\vdots \\ \tilde{\mathrm{g}}^{(2)}_{\theta_R}(\tau_m) &= \mathrm{g}^{(2)}_{\theta_R}(\tau_m) + n_R(m), \quad m = 1, \cdots, M_R \;, \end{aligned} \tag{3}$$

where $\mathrm{g}^{(2)}_{\theta_r}(\tau_m)$ is the noise-free ACF related to the PSD by (1) and (2). The noise $n_r(m)$ is assumed to be independent and normally distributed with zero mean and variance $\sigma^2_{n,r}$ at the angle θ_r. The PSD modelled by a GM model is expressed as

$$f(D) = \sum_{i=1}^{k} \frac{w_i}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{(D-\mu_i)^2}{2\sigma_i^2}\right), \tag{4}$$

where k is an unknown number of components and w_i, μ_i and σ_i are the weight, mean and standard deviation (STD) of the ith normal component (mode), respectively. All these parameters are to be estimated except w_k that will take the value $(1 - \sum_{i=1}^{k-1} w_i)$ since we have $\sum_{i=1}^{k} w_i = 1$.

For notation, we use: $\boldsymbol{w} = [w_1, \cdots, w_{k-1}]^T$, $\boldsymbol{\mu} = [\mu_1, \cdots, \mu_k]^T$ with $\mu_1 < \cdots < \mu_k$, $\boldsymbol{\sigma} = [\sigma_1, \cdots, \sigma_k]^T$, $\boldsymbol{\sigma^2_n} = \left[\sigma^2_{n,1}, \cdots, \sigma^2_{n,R}\right]^T$ and $\tilde{\mathbf{g}}^{(2)} = \left[\tilde{\mathbf{g}}_1^{(2)^T}, \ldots, \tilde{\mathbf{g}}_R^{(2)^T}\right]^T$ with $\tilde{\mathbf{g}}_r^{(2)} = \left[\tilde{\mathrm{g}}^{(2)}_{\theta_r}(\tau_1), \ldots, \tilde{\mathrm{g}}^{(2)}_{\theta_r}(\tau_{M_r})\right]^T$. ^{T} is the transpose operator.

By assuming the independence between the angular measurements and taking into account the assumption of independent white Gaussian noise, the likelihood function is given by

$$p\left(\tilde{\mathbf{g}}^{(2)} | k, \boldsymbol{w}, \boldsymbol{\mu}, \boldsymbol{\sigma}, \boldsymbol{\sigma^2_n}\right) = \prod_{r=1}^{R} \left(2\pi\sigma^2_{n,r}\right)^{-\frac{M_r}{2}} \exp\left(-\frac{\chi_r^2}{2\sigma^2_{n,r}}\right), \tag{5}$$

with

$$\chi_r^2 = \sum_{m=1}^{M_r} \left(\tilde{\mathrm{g}}^{(2)}_{\theta_r}(\tau_m) - \mathrm{g}^{(2)}_{\theta_r}(\tau_m, k, \boldsymbol{w}, \boldsymbol{\mu}, \boldsymbol{\sigma})\right)^2. \tag{6}$$

The inference on the unknown parameters of interest (k, $\boldsymbol{w}$, $\boldsymbol{\mu}$ and $\boldsymbol{\sigma}$) is performed based on their joint *posterior* distribution that can be easily computed using the Bayes' rule and marginalized with respect to $\boldsymbol{\sigma^2_n}$, leading to

$$p\left(k, \boldsymbol{w}, \boldsymbol{\mu}, \boldsymbol{\sigma} | \tilde{\mathbf{g}}^{(2)}\right) \propto \frac{\prod_{r=1}^{R} \left[\chi_r^2\right]^{-\frac{M_r}{2}}}{k_{max} \prod_{i=1}^{k} \left[\mu_{max} \ln\left(\frac{\sigma_{max}}{\sigma_{min}}\right) \sigma_i\right]}, \tag{7}$$

where k_{max} is a specified maximum number of components, $\mu_{min} \leq \mu_i \leq \mu_{max}$ and $\sigma_{min} \leq \sigma_i \leq \sigma_{max}$.

Since the derived *posterior* distribution (6) is known up to a multiplicative constant and it is a function of parameters with variable dimension spaces, a reversible jump MCMC algorithm [1, 14] is used to sample this distribution. The used *prior* distributions and the RJMCMC algorithm are detailed in [1].

The parameters of the GM model of the PSD are estimated from the generated samples using the maximum a *posteriori* estimator for k, $\hat{k} = \arg\max_{k}(p(k|\tilde{\mathbf{g}}^{(2)}))$ and the *posterior* expectation conditioned to $k = \hat{k}$ for the other parameters, $\hat{\boldsymbol{w}} = E[p(\boldsymbol{w}|k = \hat{k}, \tilde{\mathbf{g}}^{(2)})]$, $\hat{\boldsymbol{\mu}} = E[p(\boldsymbol{\mu}|k = \hat{k}, \tilde{\mathbf{g}}^{(2)})]$ and $\hat{\boldsymbol{\sigma}} = E[p(\boldsymbol{\sigma}|k = \hat{k}, \tilde{\mathbf{g}}^{(2)})]$.

3. CRAMÉR-RAO BOUNDS

In this section, we derive the CRBs for the parameters estimation of the PSD GM model with a fixed number of components k. In this multivariate estimation problem, we first need to calculate the FIM that will be inverted to get the CRBs.

Let $\boldsymbol{\alpha} = [w_1, \ldots, w_{k-1}, \mu_1, \ldots, \mu_k, \sigma_1, \ldots, \sigma_k]^T$ denotes the vector of the PSD GM model parameters and $\boldsymbol{\Theta} = \left[\boldsymbol{\alpha}^T, \boldsymbol{\sigma^2_n}^T\right]^T$ denotes the vector of all parameters.

The FIM, $\mathcal{I}$, associated with this estimation problem is a $(3k-1+R) \times (3k-1+R)$ matrix with elements given by [15]

$$\mathcal{I}_{i,j} = -E\left[\frac{\partial^2 \ell\left(\tilde{\mathbf{g}}^{(2)}; \boldsymbol{\Theta}\right)}{\partial\Theta_i \partial\Theta_j}\right] \tag{8}$$

where $E[\cdot]$ is the expectation operator and $\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right)$ is the log-likelihood function given from (5) by

$$\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right) = -\sum_{r=1}^{R}\frac{M_r}{2}\log\left(2\pi\sigma_{n,r}^2\right) - \sum_{r=1}^{R}\frac{1}{2\sigma_{n,r}^2}\sum_{m=1}^{M_r}\left(\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right)^2, \quad (9)$$

The first partial derivatives are expressed as

$$\frac{\partial\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right)}{\partial\alpha_i} = \sum_{r=1}^{R}\frac{1}{\sigma_{n,r}^2}\sum_{m=1}^{M_r}\left[\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_i} \times\left(\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right)\right], \quad (10)$$

$$\frac{\partial\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right)}{\partial(\sigma_{n,r}^2)} = \frac{-M_r}{2\sigma_{n,r}^2} + \frac{1}{2\sigma_{n,r}^4}\sum_{m=1}^{M_r}\left(\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right)^2, \quad (11)$$

for $i = 1,\ldots,3k-1$ and $r = 1,\ldots,R$.

Note that from the noise assumptions (zero mean and variance $\sigma_{n,r}^2$) we have

$$E\left[\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right] = 0, \quad (12)$$

$$E\left[\left(\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right)^2\right] = \sigma_{n,r}^2. \quad (13)$$

The regularity condition is verified for all parameters since $E\left[\frac{\partial\ell(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta})}{\partial\alpha_i}\right] = 0$ and $E\left[\frac{\partial\ell(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta})}{\partial(\sigma_{n,r}^2)}\right] = 0$.

The second partial derivatives are expressed as

$$\frac{\partial^2\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right)}{\partial\alpha_i\partial\alpha_j} = \sum_{r=1}^{R}\frac{-1}{\sigma_{n,r}^2}\sum_{m=1}^{M_r}\left[\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_i}\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_j} - \frac{\partial^2 g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_i\partial\alpha_j}\left(\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right)\right], \quad (14)$$

$$\frac{\partial^2\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right)}{\partial\alpha_i\partial(\sigma_{n,r}^2)} = \frac{-1}{\sigma_{n,r}^4}\sum_{m=1}^{M_r}\left[\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_i} \times\left(\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right)\right], \quad (15)$$

$$\frac{\partial^2\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right)}{\partial(\sigma_{n,r}^2)^2} = \frac{Mr}{2\sigma_{n,r}^4} - \frac{1}{\sigma_{n,r}^6}\sum_{m=1}^{M_r}\left(\tilde{g}_{\theta_r}^{(2)}(\tau_m) - g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})\right)^2, \quad (16)$$

$$\frac{\partial^2\ell\left(\tilde{\mathbf{g}}^{(2)};\mathbf{\Theta}\right)}{\partial(\sigma_{n,r_1}^2)\partial(\sigma_{n,r_2}^2)} = 0, \quad (17)$$

for $i,j = 1,\ldots,3k-1$ and $r,r_1,r_2 = 1,\ldots,R$ with $r_1 \neq r_2$.

Finally, the resulting expressions of the FIM elements are given by

$$\mathcal{I}_{\alpha_i,\alpha_j} = \sum_{r=1}^{R}\frac{1}{\sigma_{n,r}^2}\sum_{m=1}^{M_r}\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_i}\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_j}, \quad (18)$$

$$\mathcal{I}_{\alpha_i,\sigma_{n,r}^2} = 0, \quad (19)$$

$$\mathcal{I}_{\sigma_{n,r}^2,\sigma_{n,r}^2} = \frac{M_r}{2\sigma_{n,r}^4}, \quad (20)$$

$$\mathcal{I}_{\sigma_{n,r_1}^2,\sigma_{n,r_2}^2} = 0, \quad (21)$$

for $i,j = 1,\ldots,3k-1$ and $r,r_1,r_2 = 1,\ldots,R$ with $r_1 \neq r_2$. The expression of $\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_i}$ is given in appendix A.

Since the elements $\mathcal{I}_{\alpha_i,\sigma_{n,r}^2}$ and $\mathcal{I}_{\sigma_{n,r_1}^2,\sigma_{n,r_2}^2}$ of the FIM are zero, we can consider only the block of elements $\mathcal{I}_{\alpha_i,\alpha_j}$ in the FIM inversion. The Cramér-Rao Bounds of the PSD GM model parameters, α_i, are given by the formula

$$\mathrm{CRB}(\alpha_i) = \mathcal{I}_{\alpha_i,\alpha_i}^{-1}. \quad (22)$$

Note that it is hard to get the analytical expressions of the CRBs from the derived FIM. In this case, the integrals computation to calculate $\frac{\partial g_{\theta_r}^{(2)}(\tau_m,\boldsymbol{\alpha})}{\partial\alpha_i}$ (see (25) in appendix A) and the FIM inversion should be done numerically.

As it is known, if $\hat{\alpha}_i$ is any unbiased estimator of the parameter α_i, $\mathrm{CRB}(\alpha_i)$ is the lower bound to the mean square error (MSE) of this estimator and we have

$$\mathrm{MSE}(\hat{\alpha}_i) \geq \mathrm{CRB}(\alpha_i), \quad (23)$$

where the mean square error is defined as

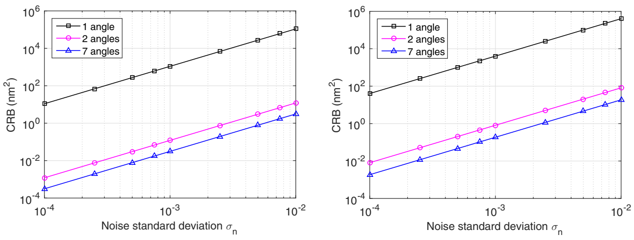
$$\mathrm{MSE}(\hat{\alpha}_i) = E[(\hat{\alpha}_i - \alpha_i)^2]. \quad (24)$$

4. RESULTS AND DISCUSSION

In this section, obtained results with simulated MDLS data are presented. For sake of space, only results for monomodal PSD will be presented. The considered PSD is a Gaussian distribution with a mean $\mu = 500$ nm and an STD $\sigma = 10$ nm.

MDLS data were simulated by considering latex particles with refractive index 1.59, dispersed in pure water (refractive index 1.33 and viscosity $\eta = 0.89$ mPa.s). The considered laser light is vertically-polarized with a wavelength $\lambda_0 = 638$ nm. The temperature is fixed at 298.15 K. For each angle, the simulated intensity ACF were computed for 160 points of τ logarithmically spaced between 1 µs and 0.7 s.

First, we illustrate the usefulness of multiangle DLS in decreasing the CRBs. Figure 1 shows the comparison of the CRBs for different sets of angles $\{\theta_r,\ r = 1,\ldots,R\}$: 1 angle (90°), 2 angles (60°, 90°) and 7 angles (60°:10°:120°). Figure 1(a) shows the CRB of the PSD mean estimation while Figure 1(b) shows that of the PSD STD estimation. The CRBs



(a) CRB of the PSD mean μ (b) CRB of the PSD STD σ

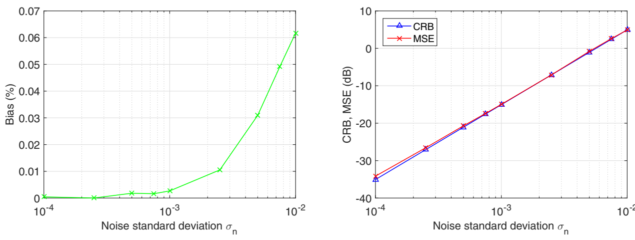
Fig. 1. Comparison of the CRBs for the estimation of a monomodal PSD (μ = 500 nm, σ = 10 nm) from MDLS data with different sets of angles: 1 angle (90°), 2 angles (60°, 90°) and 7 angles (60°:10°:120°).

are determined for different values of the noise standard deviation, $\sigma_{n,r}$. For sake of simplicity, the data for all the angles in each set were supposed to have the same $\sigma_{n,r} = \sigma_n$. For single-angle DLS, the results show that the lower bounds are relatively high. The results show also that multiangle DLS significantly decreases the lower bounds. For MDLS with only two angles, the CRBs are decreased by a factor $\sim 10^{-4}$ and they can be decreased more by increasing the measurements angles. Decreasing the CRBs by multiangle DLS has been also noticed for multimodal PSDs.

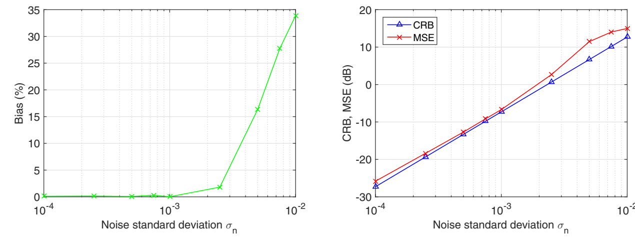
Note that for multimodal PSDs, processing DLS data from only two angles may not be sufficient for reducing significantly the CRBs. The authors of [12] have suggested to choose at least 5 angles from as wide a range of angles as possible. This is why the set of scattering angles will be fixed hereafter to 7 angles between 60° and 120° with a step of 10°.

To statistically assess the robustness of the proposed Bayesian method (RJMCMC) in [1], the performance of the PSD GM model parameters estimation are evaluated through simulated data. First, the noise-free time ACFs $g_{\theta_r}^{(2)}(\tau_m)$ were simulated from the corresponding PSD using (1) and (2). Then, the noisy time ACFs $\tilde{g}_{\theta_r}^{(2)}(\tau_j)$ were simulated by adding a noise with the same standard deviation, σ_n, for all the scattering angles as in (3). The RJMCMC algorithm has been run with the following settings, $k_{max} = 5$, $\mu_{max} = 2000$ nm, $\sigma_{min} = 0.2$ nm and $\sigma_{max} = 200$ nm. The parameter estimates are extracted from 200000 sweeps after a burn-in period of 50000 sweeps.

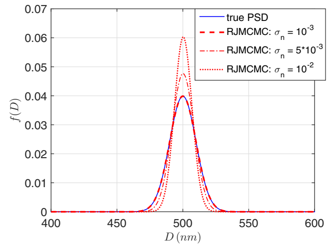
The performance indexes (Bias and MSE) of the PSD mean and standard deviation estimates by the RJMCMC were computed using 500 Monte Carlo simulations of noise for different values of σ_n. The obtained results are reported in Figure 2. Figure 2(a) shows the relative absolute bias of the PSD mean estimator, $\frac{100|E[\hat{\mu}]-\mu|}{\mu}$. As one can notice, the PSD mean estimator is unbiased since the bias is almost zero. Figure 2(b) displays the comparison between the CRB and the MSE of the PSD mean estimator. The results show that the



(a) Relative absolute bias of $\hat{\mu}$ (b) CRB vs MSE of $\hat{\mu}$



(c) Relative absolute bias of $\hat{\sigma}$ (d) CRB vs MSE of $\hat{\sigma}$



(e) The true PSD compared to the estimated ones by the RJMCMC

Fig. 2. Performances of the PSD estimation with the RJMCMC [1] for a simulated monomodal PSD (μ = 500 nm, σ = 10 nm) from MDLS data with a set of 7 angles (60°:10°:120°).

MSE of the PSD mean estimator reaches the CRB.

The relative absolute bias of the PSD standard deviation (STD) estimator, $\frac{100|E[\hat{\sigma}]-\sigma|}{\sigma}$, is shown in Figure 2(c). The PSD STD estimator is unbiased for $\sigma_n \leq 10^{-3}$. For $\sigma_n > 10^{-3}$, the bias increases with increasing σ_n. The comparison between the CRB and the MSE of the PSD STD estimator is shown in Figure 2(d). For $\sigma_n \leq 10^{-3}$ where the estimator is unbiased, the MSE is very close to the CRB with a small difference of 0.6 dB.

The reconstructed PSDs using (4) with the estimated parameters for different values of σ_n are shown in Figure 2(e) and compared to the true PSD. For $\sigma_n \leq 10^{-3}$, the estimated PSD is close to the true PSD. For $\sigma_n > 10^{-3}$, the estimated PSD becomes narrower with increasing σ_n.

To sum up, the PSD mean estimator using the proposed method [1] achieves the CRB for the monomodal PSD. Moreover, the MSE of the PSD STD estimator achieves the CRB when its bias reaches zero. This illustrates the robustness of the proposed method.

5. CONCLUSION

The Cramér-Rao lower Bounds for parametric estimation of the number-weighted particle size distribution with a Gaussian mixture model from multiangle dynamic light scattering measurements is derived. It is shown that multiangle DLS significantly decreases the CRBs. The analysis of simulated monomodal PSD data using the Bayesian inference method proposed in [1] was presented. The results have shown that the MSE of the PSD GM model parameter estimates achieves the derived CRBs of these parameters. Results on the CRBs for multimodal PSDs will be presented in future work.

A. APPENDIX

The partial derivative of $\mathrm{g}_{\theta_r}^{(2)}(\tau_m, \boldsymbol{\alpha})$ with respect to α_i in the FIM expression (18) can be derived from (1) and (2):

$$\begin{aligned}\frac{\partial \mathrm{g}_{\theta_r}^{(2)}(\tau_m, \boldsymbol{\alpha})}{\partial \alpha_i} &= \frac{2\beta}{k_{\theta_r}^3}\int_0^\infty f(D)C_I(\theta, D)\exp(-\frac{\Gamma_0(\theta)}{D}\tau)\mathrm{d}D \\ &\times [k_{\theta_r}\int_0^\infty \frac{\partial f(D,\boldsymbol{\alpha})}{\partial \alpha_i}C_I(\theta, D)\exp(-\frac{\Gamma_0(\theta)}{D}\tau)\mathrm{d}D \\ &- \frac{\partial k_{\theta_r}}{\partial \alpha_i}\int_0^\infty f(D)C_I(\theta, D)\exp(-\frac{\Gamma_0(\theta)}{D}\tau)\mathrm{d}D], \quad (25)\end{aligned}$$

where

$$\frac{\partial k_{\theta_r}}{\partial \alpha_i} = \int_0^\infty \frac{\partial f(D,\boldsymbol{\alpha})}{\partial \alpha_i}C_I(\theta_r, D)\mathrm{d}D. \quad (26)$$

From (4) and by changing α_i by w_i, μ_i or σ_i, we have

$$\begin{aligned}\frac{\partial f(D,\boldsymbol{\alpha})}{\partial w_i} &= \frac{1}{\sqrt{2\pi}\sigma_i}\exp\left(-\frac{(D-\mu_i)^2}{2\sigma_i^2}\right) \\ &-\frac{1}{\sqrt{2\pi}\sigma_k}\exp\left(-\frac{(D-\mu_k)^2}{2\sigma_k^2}\right), \quad (27)\end{aligned}$$

for $i = 1, \ldots, k-1$, and

$$\frac{\partial f(D,\boldsymbol{\alpha})}{\partial \mu_i} = \frac{w_i}{\sqrt{2\pi}\sigma_i^3}(D-\mu_i)\exp\left(-\frac{(D-\mu_i)^2}{2\sigma_i^2}\right), \quad (28)$$

$$\frac{\partial f(D,\boldsymbol{\alpha})}{\partial \sigma_i} = \frac{w_i}{\sqrt{2\pi}\sigma_i^2}\left(-1+\frac{(D-\mu_i)^2}{\sigma_i^2}\right)\exp\left(-\frac{(D-\mu_i)^2}{2\sigma_i^2}\right), \quad (29)$$

for $i = 1, \ldots, k$.

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