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A recursive regularization algorithm for estimating the particle size distribution from multiangle dynamic light scattering measurements

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ABSTRACT

Conventional regularization methods have been widely used for estimating particle size distribution (PSD) in single-angle dynamic light scattering, but they could not be used directly in multiangle dynamic light scattering (MDLS) measurements for lack of accurate angular weighting coefficients, which greatly affects the PSD determination and none of the regularization methods perform well for both unimodal and multimodal distributions. In this paper, we propose a recursive regularization method—Recursion Nonnegative Tikhonov–Phillips–Twomey (RNNT-PT) algorithm for estimating the weighting coefficients and PSD from MDLS data. This is a self-adaptive algorithm which distinguishes characteristics of PSDs and chooses the optimal inversion method from Nonnegative Tikhonov (NNT) and Nonnegative Phillips–Twomey (NNPT) regularization algorithm efficiently and automatically. In simulations, the proposed algorithm was able to estimate the PSDs more accurately than the classical regularization methods and performed stably against random noise and adaptable to both unimodal and multimodal distributions. Furthermore, we found that the six-angle analysis in the 30–130° range is an optimal angle set for both unimodal and multimodal PSDs.

1. Introduction

Multiangle dynamic light scattering (MDLS) [1–4] is a widely used technique for measuring the size distributions of nano- and micro-particles dispersed in dilute suspension, particularly for multimodal or polydisperse samples. Compared with single-angle dynamic light scattering (DLS) measurement, MDLS provides integrated information by combining the autocorrelation functions (ACF) of light intensity measured at a number of scattering angles.

Retrieving the particle size distribution (PSD) information from MDLS measurements that are generally corrupted by noise is known as a highly ill-posed mathematical problem. To solve this kind of inverse problem, numerous approaches have been proposed, such as the regularization method [5,6], the CONTIN method [7,8], the Bayesian strategies method [9], the neural network method [10] and so on. In general, these methods work well for unimodal PSD. However, they are very noise sensitive and time-consuming. Moreover, their capacity to discriminate the peaks of multimodal distributions, which represent quite a few components of communities such as the size distribution of the phytoplankton [11], the food [12]and so on, worsens specially. Furthermore, multiangle data treatment requires appropriate angular weighting of each autocorrelation measurement, which is the key to the data analysis, prior to calculation of the PSD. The weighting coefficients may be obtained from (i) the average scattering light intensity at different angles or (ii) the autocorrelation baselines. Both methods induce measurement noise, hence intolerably corrupts the accuracy of the

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weighting coefficients, and then propagates errors to the inversion of the PSD. Therefore, the solution to the weighting coefficients is a major issue that must be solved.

Vega et al. [13,14] proposed a method that applied least-squares method to recursion procedure to estimate the angular weighting ratios and PSDs in MDLS. However the main shortcoming of this approach lies in the propagation of errors on the PSDs by least-squares method to the recursion procedure that deteriorates the estimation performance particularly for multimodal PSDs. The existing inversion approaches, such as Tikhonov [6] and Phillips–Twomey [5] regularization have been verified to improve the veracity of the inversion results. However, neither algorithm suits both unimodal and multimodal distributions and could be applied directly to the inversion problem for MDLS unless they could be combined with the method for estimating the weighting coefficients.

In this paper, we propose a recursive regularization algorithm, henceforth will be called Recursion Nonnegative Tikhonov–Phillips–Twomey (RNNT-PT) algorithm, where nonnegative Tikhonov (NNT) or nonnegative Phillips–Twomey (NNPT) regularization method is followed by a recursion step to reconstruct the PSD from MDLS data, according to the inversion characteristics of the two regularization methods for different distributions. The innovation of the RNNT-PT algorithm is that using the recursion procedure for estimating the weighting coefficients and choosing the optimal inversion method for different PSDs from NNT and NNPT regularization efficiently and automatically. And we present the most appropriate number and span of scattering angles. We show that the RNNT-PT algorithm can be applied satisfactorily to the inverse problem of MDLS and is stable against random noise and adaptable to both unimodal and multimodal distributions.

2. The theory of MDLS

At a series of given scattering angle θ_r of the MDLS measurement [15], digital correlator data recorded consist of (second order) autocorrelation function of the scattered light intensity, $G^{(2)}_{\theta_r}(\tau_j)$. τ_j is the delay time at channel j. $G^{(2)}_{\theta_r}(\tau_j)$ is related to the (first-order and normalized) autocorrelation function of the electric field, $g^{(1)}_{\theta_r}(\tau_j)$.

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

where $G^{(2)}_{\infty,\theta_r}$ is the autocorrelation baseline, β (<1) is an instrumental constant, R is the number of measured angles, M_r is the number of correlator channels at θ_r. The autocorrelation function of the electric field, $g^{(1)}_{\theta_r}(\tau_j)$, is determined by particle size distribution $f(D_i)$,

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

with

$$\Gamma_0=\frac{16\pi n^2K_BT}{3\eta\lambda^2}\sin^2(\frac{\theta_r}{2}) \tag{3}$$

Here λ (nm) is the in vacuo wavelength of the incident laser light; n is the real refractive index of the non-absorbent medium; $K_B(=1.38\times10^{-23}J/K)$ is the Boltzmann constant; T (K) is the absolute temperature; $\eta(g/\text{nms})$ is the medium viscosity; $C_{I,\theta_r}(D_i)$ represents the fraction of scattering light intensity by a particle of diameter D_i at θ_r and it is calculated through the Mie theory [16]; $f(D_i)(i=1,2,...,N)$ is the discrete PSD and N is the number of PSD points, which are evenly spaced in the range $[D_{min},D_{max}]$; and k_{θ_r} is the weighting coefficients at a given scattering angle.

In vectorial notation, Eq. (2) can be lumped into the single expression

$$\mathbf{g}^{(1)}_r=k_{\theta_1}\mathbf{G}_r\mathbf{f} \tag{4}$$

where the augmented vector $\mathbf{g}^{(1)}_r=(\mathbf{g}^{(1)}_{\theta_1},\mathbf{g}^{(1)}_{\theta_2},...,\mathbf{g}^{(1)}_{\theta_r})^T$with dimension $[(M_1+...+M_r)\times1]$, and $\mathbf{g}^{(1)}_{\theta_r}$ $(M_r\times1)$ contains elements of $\mathbf{g}^{(1)}_{\theta_r}(\tau_j)$, τ_j is the delay time at channel j $(j=1,2,...,M_r)$; the augmented matrix $\mathbf{G}_r=(k^*_{\theta_1}\mathbf{F}_{\theta_1},k^*_{\theta_2}\mathbf{F}_{\theta_2},...,k^*_{\theta_r}\mathbf{F}_{\theta_r})^T$ with dimension $[(M_1+...+M_r)\times \text{N}]$, $\mathbf{F}_{\theta_r}$ that is an $(M_r\times N)$ matrix contains elements of $e^{-\Gamma_0(\theta_r)\tau_j/D_i}\cdot C_{I,\theta_r}(D_i)$, which can be calculated through the Mie theory; k_{θ_1} is the weighting coefficient at the reference angle θ_1; $\mathbf{f}$ $(N\times1)$ represents the vector containing elements of $f(D_i)$. Theoretically, if a set of $g^{(1)}_{\theta_r}(\tau_j)$ $(r\in[1,R])$ is provided, $f(D_i)$ should be achieved by Eq. (4). However, this is usually an ill-posed mathematical problem. The reconstructed result is greatly influenced by a dimensionless weighting coefficient ratio $k^*_{\theta_r}$ that is defined by Eq. (5) [14]

$$k^*_{\theta_r}=\frac{k_{\theta_r}}{k_{\theta_1}}=\left(\frac{N_{p,\theta_r}}{N_{p,\theta_1}}\right)\left[\frac{G^{(2)}_{\infty,\theta_1}}{G^{(2)}_{\infty,\theta_r}}\right]^{1/2}=\left(\frac{N_{p,\theta_r}}{N_{p,\theta_1}}\right)\frac{\langle I_{\theta_1}\rangle}{\langle I_{\theta_r}\rangle} \tag{5}$$

Here $N_{p,\theta_r}/N_{p,\theta_1}$ is the ratio between particle concentration at θ_r and particle concentration at θ_1. If the sample concentration keeps invariable at different scattering angles, $N_{p,\theta_r}/N_{p,\theta_1}=1$. $\langle I_{\theta_r}\rangle$ is the mean intensity scattered at angle θ_r.

By definition, $k^*_{\theta_1}=1$. Eq. (4) must be solved for $k_{\theta_1}\mathbf{f}$, and for the remaining $(R-1)$ unknown $k^*_{\theta_r}$'s. Since k_{θ_1} does not affect the distribution of $\mathbf{f}$, we set $k_{\theta_1}=1$ for simplicity. We here proposed the following solution: first, estimate the weighting coefficient ratio $k^*_{\theta_r}$, and then find $\mathbf{f}$ by the inversion of Eq. (4).

3. Pre-processing and RNNT-PT method

3.1. Pre-processing

Assume that autocorrelation function of the scattered light intensity measurements, $\text{G}^{(2)}_{\theta_r}$, are available ($r$=1,…,$R$). As schematically represented in Fig. 1(a), the pre-processing involves two parts: (1) the calculation of the r secondary measurements, $\mathbf{g}^{(1)}_{\theta_r}$ and the vector $\mathbf{g}^{(1)}_r$ and by the similar process, we get $\mathbf{g}^{(1)}_{\theta_{r+1}}$ and the vector $\mathbf{g}^{(1)}_{r+1}$, through Eqs. (1) and (2) the calculation of Mie theory to