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Angular dependence of multiangle dynamic light scattering for particle size distribution inversion using a self-adapting regularization algorithm

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The multiangle dynamic light scattering (MDLS) technique can better estimate particle size distributions (PSDs) than single-angle dynamic light scattering. However, determining the inversion range, angular weighting coefficients, and scattering angle combination is difficult but fundamental to the reconstruction for both unimodal and multimodal distributions. In this paper, we propose a self-adapting regularization method called the wavelet iterative recursion nonnegative Tikhonov–Phillips–Twomey (WIRNNT-PT) algorithm. This algorithm combines a wavelet multiscale strategy with an appropriate inversion method and could self-adaptively optimize several noteworthy issues containing the choices of the weighting coefficients, the inversion range and the optimal inversion method from two regularization algorithms for estimating the PSD from MDLS measurements. In addition, the angular dependence of the MDLS for estimating the PSDs of polymeric latexes is thoroughly analyzed. The dependence of the results on the number and range of measurement angles was analyzed in depth to identify the optimal scattering angle combination. Numerical simulations and experimental results for unimodal and multimodal distributions are presented to demonstrate both the validity of the WIRNNT-PT algorithm and the angular dependence of MDLS and show that the proposed algorithm with a six-angle analysis in the 30–130° range can be satisfactorily applied to retrieve PSDs from MDLS measurements.

1. Introduction

Many novel and useful techniques have emerged as powerful tools to measure particle size distribution (PSD) such as the light scattering technology, the scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FT-IR) and so on. Light scattering is a versatile and non-invasive set of technique for measuring in situ on PSD. With the development of multiangle light scattering (MALS) measuring systems [1–3], multiangle dynamic light scattering (MDLS) and multiangle static light scattering (MSLS) [4–6] are widely applied to measure PSD of a variety of systems like emulsions, polymers, vesicles. For the determination of nano- or submicron particle size, MDLS should provide a better estimate of PSD than MSLS, which focuses on the determination of PSD in the larger size range from roughly 0.1 to a few micrometers. MDLS, which consists of acquiring the autocorrelation functions (ACFs) of light intensity at several different angles and processing the whole set of collected information, has become a promising technique to assess the PSD of a sample dispersed in a dilute suspension, particularly for polydisperse or multimodal samples. As the properties of nano- and submicron particles are influenced by their size, many fields of research require estimating the PSD with good resolution, ranging from the study of the process control of nanoparticle growth [7–9] and protein aggregation [10,11] to the monitoring of atmospheric aerosols [12–15] and the combustion processes of soot and fuels [16–18].

Retrieving the PSD from MDLS measurements, i.e., acquiring the exact solution of a Fredholm integral equation of the first kind, is a well-known ill-posed problem that is considered highly complex since the solution lacks uniqueness and existence; in other words, the presence of a small amount of noise in the measured angular light-scattering data can give rise to large spurious oscillations in the solution. Numerous inverse techniques, such as the Bayesian method [19], the CONTIN method [20,21], the regularization method [22,23] and the neural network method [24], have been developed to retrieve the PSD from MDLS data. The main drawback of these methods is the poor capacity to discriminate the peaks of multimodal PSDs. Moreover, these methods have

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unsatisfactory stability in the presence of random noise and are time consuming. Other noteworthy issues with the data inversion for MDLS lie in the determination of the inversion range, the angular weighting coefficients and the scattering angle combination, which greatly affect the estimation of PSDs. For all the above inversion methods, if a good inversion range cannot be provided, the parameter optimization process often becomes trapped into local minima, which leads to large errors. Wavelet multiscale analysis is a newly developed inversion strategy to accelerate convergence, avoid disturbance of the local minimum and enhance the stability and reliability of inversion. Its effectiveness has been demonstrated for many inverse problems involving the nonlinear geophysics equation [25], the two-dimensional acoustic wave equation [26] and ill-posed equations [27] such as that in the main problem to be resolved in this paper. For the second issue, the weighting coefficients may be directly obtained from (i) the average scattering light intensities at different angles or (ii) the autocorrelation baselines. However, the propagation of errors associated with such experimental methods, which inevitably induce noise, may intolerably corrupt the PSD estimate. To obtain more precise weighting coefficients, Vega et al. [28,29] proposed a recursive method based on a least-squares calculation, and we further improved this method by introducing nonnegative Tikhonov [23] (NNT) and nonnegative Phillips-Twomey [22] (NNPT) regularization methods in each recursion step in our previous study [30]; the resulting algorithm was called the recursion nonnegative Tikhonov-Phillips-Twomey (RNNT-PT) algorithm and was validated with simulated MDLS data for unimodal and multimodal PSDs. Regarding the third issue, despite the clear importance of choosing measurement angles in MDLS, they are rarely studied and analyzed in simulations or experiments, nor are referable angle numbers and ranges provided.

In the present work, we propose a self-adapting regularization method called the wavelet iterative recursion nonnegative Tikhonov–Phillips–Twomey (WIRNNT-PT) algorithm and provide a recommended angle combination—a six-angle analysis in the 30–130° range—to improve estimates of the weighting coefficients and the PSDs. The whole inversion process is conducted using a wavelet multiscale strategy, and the inversions are carried out at different scales by an appropriate reconstruction method. In this method, an iterative step is developed from our previous recursion method [30], and the optimal inversion method is automatically chosen from NNT or NNPT regularization in each iterative recursion step on the basis of research on the inversion peculiarities of the two regularization methods for different distributions.

The basic theoretical principles of MDLS and the proposed WIRNNT-PT algorithm are presented in Sections 2 and 3, respectively. Section 4 provides insights into the results obtained when the proposed method is applied to simulated and experimental data, as well as comparisons with the RNNT-PT methods. Section 5 presents a thorough analysis of the angular dependence of the MDLS for estimating PSDs.

2. Theory of MDLS

In DLS, a devoted digital correlator enables measuring the second-order autocorrelation function of the light scattered at a given θ_r, $G^{(2)}_{\theta_r}(\tau_j)$, and for different values of the time delay, τ_j. In MDLS [31], several measurements are taken at different θ_r(r = 1, 2, ..., R). These measurements are related to the (first-order and normalized) autocorrelation function of the electric field, $g^{(1)}_{\theta_r}(\tau_j)$.

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

where $G^{(2)}_{\infty,\theta_r}$ is the measured baseline, β (<1) is an instrumental parameter, R is the total number of scattering angles, and M_r is the total number of points of the autocorrelation functions (limited by the number of available correlator channels). For a given angle, the autocorrelation function of the electric field, $g^{(1)}_{\theta_r}(\tau_j)$, is determined by the PSD $f(D_i)$ as follows:

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

with

$$\Gamma_0 = \frac{16\pi n^2 K_B T}{3\eta\lambda^2}\sin^2\left(\frac{\theta_r}{2}\right), \tag{3}$$

$$k_{\theta_r} = \frac{1}{\sum_{i=1}^{N} C_{I,\theta_r}(D_i)f(D_i)}\quad (r = 1, 2, ..., R) \tag{4}$$

where k_{θ_r} are (a priori unknown) the weighting coefficients at each given scattering angle, θ_r, and the denominator of Eq. (4) is proportional (but not equal) to the light intensity scattered at θ_r, thus the k_{θ_r} are proportional to both $\langle I_{\theta_r}\rangle^{-1}$ and $(\sqrt{G^{(2)}_{\infty,\theta_r}})^{-1}$; $C_{I,\theta_r}(D_i)$ represents the fraction of scattering light intensity by a particle of diameter D_i at θ_r, which can be calculated through Mie scattering theory [32]; $f(D_i)(i = 1, 2, ..., N)$ is the discrete PSD, and N is the number of PSD points, which are evenly spaced in the range $[D_{\min}, D_{\max}]$; λ(nm) is the in vacuo wavelength of the incident laser light; n is the real refractive index of the nonabsorbent medium; $K_B(= 1.38\times10^{-23}$J/K) is the Boltzmann constant; T(K) is the absolute temperature, and η(g/nms) is the medium viscosity at T.

Then, for the most general case, Eq. (2) gives rise to a matrix equation of the form

$$\mathbf{g}^{(1)}_r = k_{\theta_1}\mathbf{G}_r\mathbf{f}, \tag{5}$$

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 dimensions $[(M_1 + ... + M_r)\times 1]$, and the elements of $\mathbf{g}^{(1)}_{\theta_r}$ $(M_r\times 1)$ are $\mathbf{g}^{(1)}_{\theta_r}(\tau_j)$, where τ_j is the delay time at channel j ($j = 1, 2, ..., M_r$); k_{θ_1} is the weighting coefficient at the reference angle θ_1; $\mathbf{f}$ $(N\times 1)$ is the unknown vector that contains the fraction of particles in each size interval, $f(D_i)$; and 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 dimensions $[(M_1 + ... + M_r)\times N]$, where $\mathbf{F}_{\theta_r}$ is a an $M_r\times N$ matrix that contains elements $e^{-\Gamma_0(\theta_r)\tau_j/D_i}\cdot C_{I,\theta_r}(D_i)$, which can be calculated according to Mie theory. Recovering $\mathbf{f}$ from Eq. (5) requires accurately deriving the dimensionless weighting coefficient ratio $k^*_{\theta_r}$ relative to the fixed reference angle θ_1 as

$$k^*_{\theta_r} = \frac{k_{\theta_r}}{k_{\theta_1}} = \left(\frac{N_{p,\theta_r}}{N_{p,\theta_1}}\right)\left[\frac{G^{(2)}_{\infty,\theta_1}}{G^{(2)}_{\infty,\theta_r}}\right]^{1/2} = \left(\frac{N_{p,\theta_r}}{N_{p,\theta_1}}\right)\frac{\langle I_{\theta_1}\rangle}{\langle I_{\theta_r}\rangle}. \tag{6}$$

Here, $\langle I_{\theta_r}\rangle$ is the mean intensity scattered at angle θ_r and is related to $G^{(2)}_{\infty,\theta_r}$ through $\langle I_{\theta_r}\rangle = \sqrt{G^{(2)}_{\infty,\theta_r}}$. $N_{p,\theta_r}/N_{p,\theta_1}$ is the ratio between the particle number concentration at θ_r and the particle number concentration at θ_1. For most cases, the sample concentration remains unaltered along the measurement angles, and thus, $N_{p,\theta_r}/N_{p,\theta_1} = 1$. The autocorrelation baselines, $G^{(2)}_{\infty,\theta_r}$, or the average scattering light intensity at different angles, $\langle I_{\theta_r}\rangle$, might be considered very powerful for obtaining the weighting coefficient ratio $k^*_{\theta_r}$, according to Eq. (6) and then finding $\mathbf{f}$ by the inversion of Eq. (5). This, however, is not the case. The baseline is difficult to achieve by the above method because recovery of the PSD from MDLS is an inherently ill-posed problem, where small noises present in the