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将噪声作为独立变量的动态光散射数据反演

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摘　要:在动态光散射颗粒测量时,为了从含噪的自相关函数数据中准确地反演出颗粒粒度分布,对Tikhonov正则化算法进行改进,将噪声作为一个独立的未知变量应用到正则化方程中进行粒度反演.在计算过程中,相应增加方程中各系数矩阵的行数和列数,对求解的粒度分布数值则仍取其原来方程的行数和列数,从而达到对部分噪声的剔除作用.不同噪声水平下的颗粒粒度反演结果表明,改进后的算法能够显著提高低信噪比动态光散射数据粒度反演结果的准确性,适用于宽分布较大粒径的颗粒粒度反演.

关键词:光散射;粒度分布;颗粒测量;反问题;信噪比;噪声分离

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Inversion of Dynamic Light Scattering Data by Treating Noise as an Independent Variable

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Abstract: In dynamic light scattering measurements, noise often makes inversion of the autocorrelation function to obtain the particle size distribution unreliable. To obtain accurate particle size distributions from noisy dynamic light scattering data, a modified inversion method based on the original Tikhonov regularization algorithm is proposed. In the method, the noise in the data is considered an independent variable. During the inversion process the number of rows and columns of the coefficient matrix equation is increased to accommodate this. Finally, using the dimensions of the coefficient matrix, the poor particle size distribution data is separated from the recovered particle size distributions, reducing the influence of noise in the data. The particle size distributions recovered from the dynamic light scatteringdata show that the modified Tikhonov regularization inversion algorithm can give rise to improved accuracy compared with the original inversion algorithm, especially for low signal-to-noise ratio data.

Key words: Light scattering; Particle size distribution; Particle size analysis; Inverse problems; Signal to noise ratio; Noise separation

OCIS Codes: 290.0290;290.5820;290.5850;120.5820

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0 Introduction

Dynamic Light Scattering (DLS) is a major method for submicron particle size measurement [1-4]. In DLS measurements, noise is inevitable, and attention has to be paid to minimize the effect of noise to acquire high quality data. In 1983, Schatzel[5] investigated noise in photon correlation and photon structure functions, and in 1988 he and colleagues[6] proposed photon correlation measurements at large lag times to improve statistical accuracy. Subsequently, others have considered the effect of noise on the Autocorrelation Function (ACF) curves[7] and its effect on particle size measurement with DLS[8]. These efforts were aimed at minimizing noise during the DLS measurement. Given that the ACFs always contain noise at some level, there is also interest in reducing this noise, or de-noising, *post priori*. Shen et al. [9] demonstrated that de-noising of DLS data using wavelet packet filtering is beneficial and leads to more accurate particle sizes being recovered.

A core problem with particle size measurement using DLS is solving a Fredholm integral equation of the first kind. Tikhonov regularization [10] is an effective method for solving ill-posed problems of this kind and is commonly used for this in DLS[11-13]. The method works by adding constraints which converts an ill-posed problem to one that has good numerical stability, in turn reducing the diversity of the inversion results. However, in these techniques, the noise in the DLS data often increases the difficulty of regularization parameter choice and affects the accuracy of the inversion results. Zhu et al. [13] used constrained regularization techniques to analyze noisy DLS data.

To improve the performance of the regularization method with noisy DLS data, in this paper, we put forward a modified inversion method, based on the original Tikhonov regularization algorithm, to get more accurate Particle Size Distribution (PSD) results from noisy ACFs.

1 Tikhonov regularization and modified regularization

For DLS from a polydisperse suspension of particles, the normalized electric field ACF is

$$g^{(1)}(\tau)=\int_0^\infty G(\Gamma)\exp(-\Gamma\tau)\mathrm{d}\Gamma \tag{1}$$

where $G(\Gamma)$ is the intensity distribution function of decay constants, Γ and τ is the delay time. For spheres the particle diameter, d_{DLS}, is related to Γ by the Stokes-Einstein equation, so that

$$d_{\mathrm{DLS}}=\boldsymbol{k}^2\frac{k_{\mathrm{B}}T}{3\pi\eta\Gamma} \tag{2}$$

where $\boldsymbol{k}$ is the magnitude of the scattering vector, k_B is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the suspending liquid.

Eq. (1) can be written in discrete form as

$$g^{(1)}(\tau)=\sum_{i=1}^{N}G(\Gamma_i)\exp(-\Gamma_i\tau) \tag{3}$$

Eq. (3) can be written as an operator equation as

$$\boldsymbol{y}=\boldsymbol{Ax} \tag{4}$$

where, $\boldsymbol{A}=\exp(-\Gamma_i\tau)$, $\boldsymbol{A}\in\boldsymbol{R}^{m\times n}$, $\boldsymbol{x}=G(\Gamma_i)$ is a $n\times1$ vector, $y=g^{(1)}(\tau)$, $\boldsymbol{g}$ is a $m\times1$ vector.

Eqs. (3) and (4) are ill-conditioned. Using a regularization algorithm the ill-posed problem and the optimization problem can be solved as follows[14]

$$\min: \|\boldsymbol{Ax}-\boldsymbol{y}\|^2+\alpha\Omega(x) \tag{5}$$

Here, the coefficient matrix is $\boldsymbol{A}\in\boldsymbol{R}^{m\times n}$ $(m\geqslant n)$; α is a regularization parameter, and $\Omega(\boldsymbol{x})$ is a stability function which is a penalty function. In reality, $G(\Gamma)$ must be non-negative and this constraint condition allows Eq. (5) to be changed to

$$\min: \|\boldsymbol{Ax}-\boldsymbol{y}\|^2+\alpha\|\boldsymbol{x}\|^2 \quad \text{s. t. } x_i\geqslant0 \tag{6}$$

which is equivalent to

$$\min: \left\|\begin{bmatrix}\boldsymbol{A}\\ \sqrt{\alpha}\boldsymbol{L}\end{bmatrix}\boldsymbol{x}-\begin{bmatrix}\boldsymbol{y}\\ 0\end{bmatrix}\right\|^2 \quad \text{s. t. } x_i\geqslant0 \tag{7}$$

where, $\boldsymbol{L}$ is the identity matrix with size of $n\times n$.

What has been described thus far is the original Tikhonov regularization algorithm. Noise affects the solution, which is not well expressed in Eq. (6). In the modified solution, where noise is incorporated into the original equation as an independent, unknown variable, Eq. (1) becomes

$$g^{(1)}(\tau)=\int_0^\infty G\left(\frac{\boldsymbol{k}^2k_{\mathrm{B}}T}{3\pi\eta d_{\mathrm{DLS}}}\right)\exp\left(-\frac{\boldsymbol{k}^2k_{\mathrm{B}}T\tau}{3\pi\eta d_{\mathrm{DLS}}}\right)\mathrm{d}\Gamma+d \tag{8}$$

where d is random noise. Eq. (4) can be written as

$$\boldsymbol{y}=\boldsymbol{Ax}+\boldsymbol{d} \tag{9}$$

To estimate the unknown variable x and d, we propose to minimize the function

$$\min: \|\boldsymbol{Ax}+\boldsymbol{d}-\boldsymbol{y}\|^2+\alpha\|\boldsymbol{x}\|^2 \quad \text{s. t. } z_i\geqslant0 \tag{10}$$

Similar to Eq. (6), Eq. (10) can be reformulated as

$$\min: \left\|\begin{bmatrix}\boldsymbol{A} & \boldsymbol{L}_d\\ \sqrt{\alpha}\boldsymbol{L} & 0\end{bmatrix}\begin{bmatrix}\boldsymbol{x}\\ d\end{bmatrix}-\begin{bmatrix}\boldsymbol{y}\\ 0\end{bmatrix}\right\|^2 \quad \text{s. t. } z_i\geqslant0 \tag{11}$$

where $\boldsymbol{L}_d$ is a $m\times1$ vectorwith elements of 1, i. e. $\boldsymbol{L}_d=(1,1,\ldots1)^{\mathrm{T}}$.

In the process of the inversion calculation, let $[x\ d]^{-1}$ be referred to as an unknown variable x^1. As the dimensions of the coefficient matrix $\boldsymbol{A}$ are $m\times n$, we pick the first n group vector out from x^1 as the new x, then the new variable x is used to select an appropriate regularization parameter to obtain the PSDs.

2 Numerical simulation and analysis of inversion results

To verify the superiority of the modified regularization algorithm, we perform numerical simulation of the DLS ACFs using Johnson's SB function to generate the underlying PSD. This function can represent all unimodal PSDs including the normal, log-normal, Rosin-Rammler and even the modified beta distribution [15]. Simulation is carried out for two size distributions: a narrow unimodal distribution with a peak at 90 nm and a broad unimodal distribution with a peak at 250 nm. The simulation data conditions are as follows: the wavelength λ of He-Ne laser is 632.8 nm, the refractive index m of the solution is 1.33, the absolute temperature T is 294K, Boltzmann constant K_B is 1.3807×10^{-23} J/K, the coefficient of viscosity η is 9.78×10^{-4} Pa·s, the scattering angle θ is 90°.

The unimodal PSDs are simulated using the following Johnson's SB function

$$f(X)=\frac{\sigma}{\sqrt{2\pi}}[t(1-t)]^{-1}\exp\left\{-0.5\left[\mu+\sigma\ln\left(\frac{t}{1-t}\right)\right]^2\right\} \tag{12}$$

where, $t=\frac{X-X_{\min}}{X_{\max}-X_{\min}}$ is the normalized size and $1\geqslant t\geqslant 0$, X is the discrete particle size, $X_{\min}$ and $X_{\max}$ are minimum and maximum particle size, respectively. μ and σ are distribution parameters which control the width and shape of the PSD. For 90 nm and 250 nm unimodal distribution, the parameters are $\mu=3.8$, $\sigma=3$, $X_{\min}=10$, $X_{\max}=400$, and $\mu=2.3$, $\sigma=1$, $X_{\min}=100$, $X_{\max}=500$, respectively. Tocompare the inversion results of the original and modified regularization method, two performance parameters, peak error E_P and distribution error E_{PSD}, are introduced. These are defined as

$$E_P=\frac{|P_1-P_2|}{P_1} \tag{13}$$

where, P_1 (peak position 1) is the peak position of the simulated PSD and P_2 (peak position 2) is the peak position of the recovered PSD, and

$$E_{PSD}=\| f_1(D_i)-f_2(D_i)\|_2 \tag{14}$$

where $f_1(Di)$ is the simulated PSD and $f_2(Di)$ is the recovered PSD. The smaller the error, the better the fit between the recovered and simulated PSDs.

During the simulation, sets of field ACFs are generated with noise added at the following levels: 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}. Noise is added to the noise-free correlation data using[13]

$$y(\tau)=g^{(2)}(\tau)+\delta\varepsilon \tag{15}$$

where, ε is a normally distributed number in the range 0~1, and δ denotes the noise level.

The data are analyzed using two different inversion methods and the regularization parameter is selected by the L curve criteria[16]. Finally, the performance parameter values at the same noise level for the two inversion methods are compared.

As can be seen in Fig. 1, when the noise level is very low (10^{-5}), the recovered PSDs are exactly the same, and close to the true PSD, for both the original and modified regularization methods. However, as the noise level increases to 10^{-4} and 10^{-3}, the PSDs from the two methods are clearly different and the one from the modified method is closer to the true underlying PSD. This can be seen in Figs. 2 and 3. Table 1 summarizes the performance results of the two algorithms for the 90nm unimodal particle size sample, and the better performance of the modified algorithm can be seen clearly.

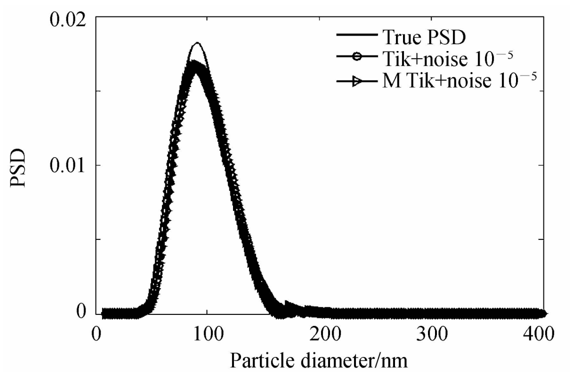

Fig. 1 The size distribution, PSD, for unimodal 90 nm particles with autocorrelation function noise of 10^{-5}

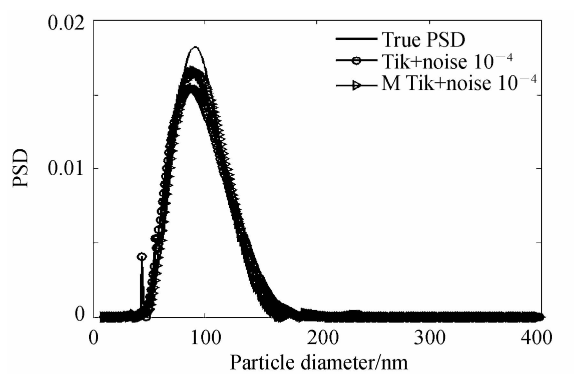

Fig. 2 The size distribution, PSD, for unimodal 90 nm particles with autocorrelation function noise of 10^{-4}

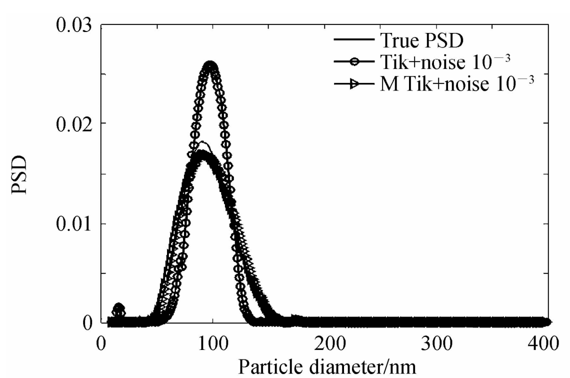

Fig. 3 The size distribution, PSD, for unimodal 90 nm particles with autocorrelation function noise of 10^{-3}

Table 1 The performance parameters of particle size distribution recovery for unimodal 90 nm particles under different autocorrelation function noise levels

Noise Level	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
Original algorithm E_P	1.1%	4.4%	4.4%	4.4%	30%
Modified algorithm E_P	1.1%	1.1%	2.2%	0	4.4%
Original algorithm E_{PSD}	0.009	0.017	0.03	0.18	0.27
Modified algorithm E_{PSD}	0.008	0.009	0.008	0.082	0.16

At 10^{-4} noise level the peak error is four times smaller and the distribution error is two times smaller for the modified algorithm compared with that of the original algorithm. The superior performance of the modified algorithm is even more apparent at higher noise levels, as can be seen from Table 1 and Figs. 4 and 5. This is especially so at 10^{-2} noise level, where using the modified method eliminates the influence of noise on the peak. At 10^{-1} noise level, the PSD recovered from the original Tikhonov method is quite different from the true PSD, whereas the PSD from the modified method is similar to the true PSD but shifts to smaller sizes and is a little narrower.

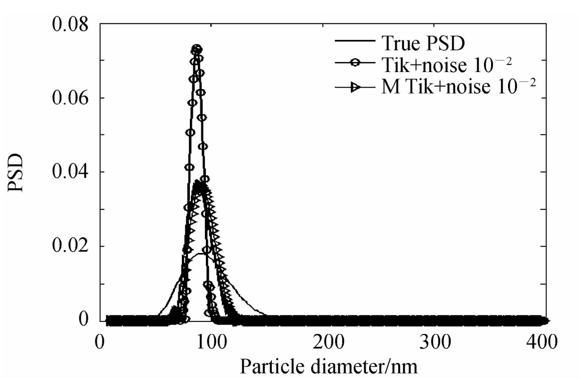

Fig. 4 The size distribution, PSD, for unimodal 90 nm particles with autocorrelation function noise of 10^{-2}

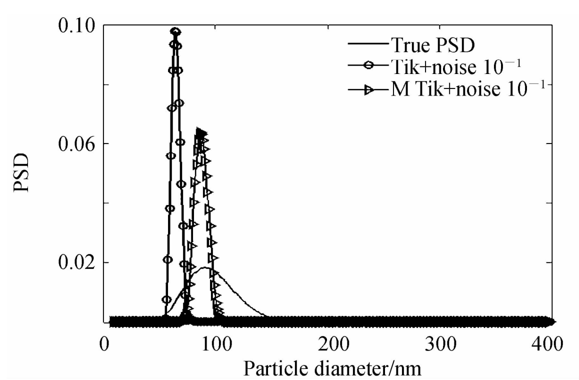

Fig. 5 The size distribution, PSD, for unimodal 90 nm particles with autocorrelation function noise of 10^{-1}

For the 250 nm unimodal sample it can be seen that the PSD results are similar to those for the 90 nm sample. As the ACF noise level increases, the modified algorithm gives better performance than the original Tikhonov algorithm. Fig. 7 and Fig. 8 show that when the noise level reaches 10^{-4} and 10^{-3}, the inversion results of the modified method compared with the original Tikhonov inversion method have been greatly improved, and the modified method eliminates the influence of noise on the peak. The performance parameters summarized in Table 2 show that both the peak error and the distribution error are markedly smaller for the modified algorithm when the noise level is 10^{-4} or greater. It can also be seen in Figs. 6～10 that the PSD obtained from the modified algorithm is closer to the true PSD than that obtained from the original Tikhonov algorithm. Comparing the PSD results forthe 250 nm sample (Figs. 6～10) with that of the 90nm sample (Figs. 1～5), it can be seen that for larger particle size and a wider distribution, ACF noise has a greater effect on the recovered PSD. From Tables 1 and 2 we see that using the modified method, gives relatively better improvement in the PSD recovery results for the 250 nm wide distribution than for the 90 nm narrow distribution.

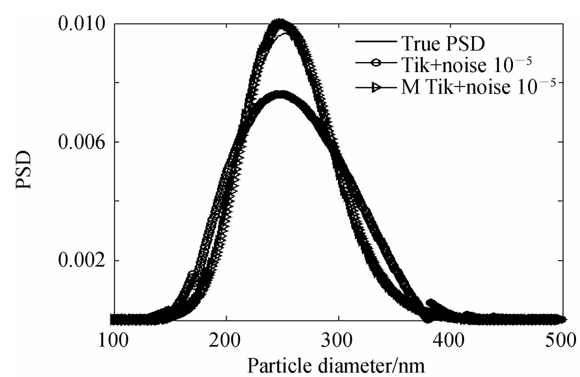

Fig. 6 The size distribution, PSD, for unimodal 250 nm particles with autocorrelation function noise of 10^{-5}

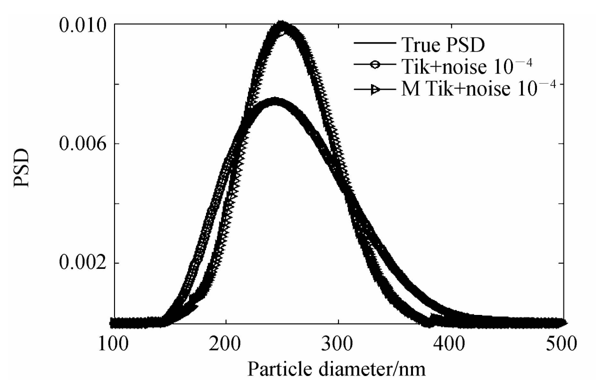

Fig. 7 The size distribution, PSD, for unimodal 250 nm particles with autocorrelation function noise of 10^{-4}

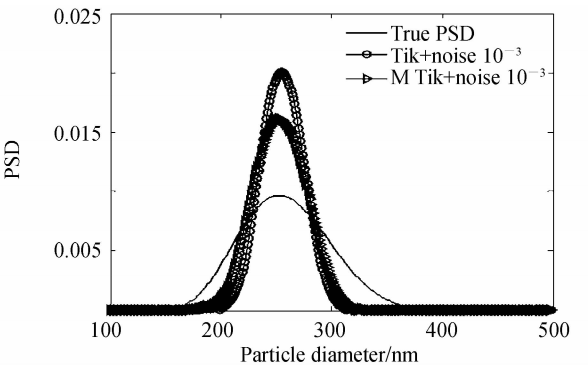

Fig. 8 The size distribution, PSD, for unimodal 250 nm particles with autocorrelation function noise of 10^{-3}

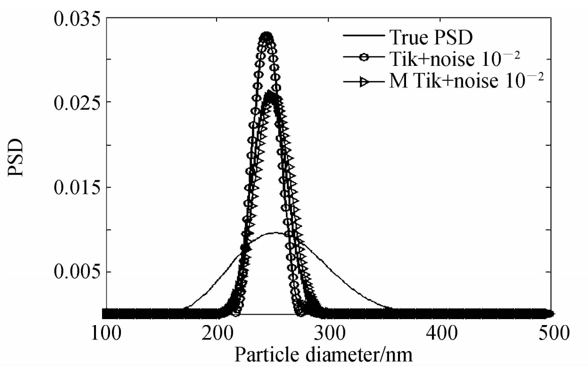

Fig. 9 The size distribution, PSD, for unimodal 250 nm particles with autocorrelation function noise of 10^{-2}

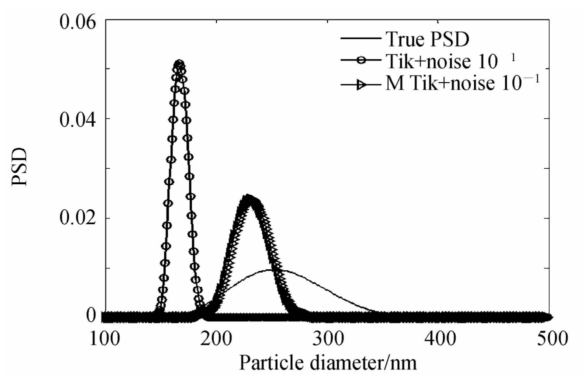

Fig. 10 The size distribution, PSD, for unimodal 250 nm particles with autocorrelation function noise of 10^{-1}

Table 2 The performance parameters of particle size distribution recovery for unimodal 250nm particles under different autocorrelation function noise levels

Noise level	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
Original algorithm E_P	1.6%	3.6%	1.2%	3.2%	34%
Modified algorithm E_P	0.8%	0	0	1.2%	8.3%
Original algorithm E_{PSD}	0.02	0.02	0.06	0.11	0.21
Modified algorithm E_{PSD}	0.004	0.003	0.04	0.09	0.09

Usually there are two kinds of signal noise in DLS data; uncorrelated noise (additive noise) and correlated noise (multiplicative noise). Eq. (15) is the relevant expression foruncorrelated noise and the expression forcorrelated noise is

$$y(\tau)=g^{(2)}(\tau)+\sqrt{\delta g^{(2)}(\tau)\varepsilon}/\delta \qquad (16)$$

where δ denotes signal-to-noise ratio.

To test the performance of the modified regularization algorithm for correlated noise, we also add noise to the ACF using Eq. (16). The PSD recovery results are similar tothose with the addition of uncorrelated noise and we conclude that the modified algorithm gives better performance also with correlated noise.

3 Conclusions

Comparing the PSD recovery results for DLS data with different levels of noise on the ACFs using two kinds of regularization inversion algorithms, we conclude that, when the noise level is high ($>\sim 10^{-5}$), the modified method, which treats noise as an independent and unknown variable, gives PSDs that are closer to the true distribution. Further, as the noise level increases, the inversion results for the modified method are better than those of the original regularization algorithm, and the former is better suited for recovering PSDs from low signal-to-noise ratio DLS data.

Comparing the inversion results for the 250 nm wide distribution and the 90 nm narrow PSDs, it can be seen that autocorrelation function noise more greatly impacts the recovered PSD for larger particle sizes and wider distributions, and the modified algorithm performs relatively better for these samples. Consequently, the modified regularization algorithm is even more suitable for the recovery of PSDs involving larger particle sizes with a wide size distribution.

Reference

[1] ZHU Xin-jun, SHEN Jin, SONG Li. Accurate retrieval of bimodal particle size distribution in dynamic light scattering [J]. *IEEE Photonics Technology Letters*, 2016, **28**(3):311-314.

[2] BALOG S, RODRIGUEZ-LORENZO L, MONNIER C A, *et al*. Characterizing nanoparticles in complex biological media and physiological fluids with depolarized dynamic light scattering[J]. *Nanoscale*, 2015, **7**(14):5991-5997.

[3] SHAN Liang, KONG Ming. Photon correlation spectroscopy for nano-particle diameter measurement with weighted nonnegative least squares[J]. *Acta Photonica Sinica*, 2013, **42**(6):684-687.

[4] YU Xiang-fei, YANG Hui, YANG Hai-ma, *et al*. An inversion algorithm of dynamic light scattering based on singular value decomposition [J]. *Acta Photonica Sinica*, 2013, **42**(11):1324-1328.

[5] SCHATZEL K. Noise in photon correlation and photon structure functions[J]. *Optica Acta: international Journal of*

Optics, 1983, **30**(2):155-166.

[6] SCHATZEL K, DREWEL M, STIMAC S. Photon correlation measurements at large lag times: improving statistical accuracy [J]. *Journal of Modern Optics*, 1988, **35**(4): 711 - 718.

[7] SMART A E, EDWARDS R V, MEYER W V. Quantitative simulation of errors in correlation analysis [J]. *Applied. Optics*, 2001, **40**(24):4064 - 4078.

[8] YANG Hui, ZHENG Gang, Li Meng-chao. A discussion of noise in dynamic light scattering for particle sizing[J]. *Particle and Particle System Characterization*, 2008, **25**(5-6): 406-413.

[9] SHEN Jin, THOMAS J C, ZHU Xin-jun, *et al*. Wavelet denoising experiments in dynamic light scattering[J]. *Optics Express*, 2011,**19**(13): 12284-12290.

[10] FUHRY M, REICHEL L. A new Tikhonov regularization method[J]. *Numerical Algorithms*, 2012, **59**(3):433-445.

[11] UBERA J V, AGUILAR J F, GALE D M. Reconstruction of particle-size distributions from light-scattering patterns using three inversion methods[J]. *Applied Optics*, 2007, **46**(1): 124-132.

[12] WANG Ya-jing, SHEN Jin, LIU Wei. Non-negative constraint research of Tikhonov regularization inversion for dynamic light scattering[J]. *Laser Physics*, 2013, **23**(8): 187-215.

[13] ZHU Xin-jun, SHEN Jin, THOMAS J C. Analysis of noisy dynamic light scattering data using constrained regularization techniques[J]. *Applied Optics*, 2012, **51**(31): 7537-7548.

[14] HAN Qiu-yan, SHEN Jin, SUN Xian-ming, *et al*. A posterior choice strategies of the Tikhonov regularization parameter in the inverse algorithm of the photon correlation spectroscopy particle sizing techniques[J]. *Acta Photonica Sinica*, 2009, **38**(11):2917-2926.

[15] TANG Hong, LIANG Guo-wei. Inversion of particle size distribution from spectral extinction data using the bimodal Johnson's SB, function[J]. *Powder Technology*, 2010, 1**98**(3):330-336.

[16] ZHU Xin-jun, SHEN Jin, LIU Wei, *et al*. Nonnegative least-squares truncated singular value decomposition to particle size distribution inversion from dynamic light scattering data[J]. *Applied Optics*, 2010, **49**(34):6591-6596.