Optics Communications 325 (2014) 71–77

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom

Photon correlation spectroscopy of the small amount of data based on auto-regressive power spectrum

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A R T I C L E I N F O

Article history:
Received 27 May 2013
Received in revised form
8 March 2014
Accepted 31 March 2014
Available online 13 April 2014

Keywords:
Photon correlation spectroscopy
Auto-regressive model
Power spectrum
Particle size measurement

A B S T R A C T

Dynamic light scattering (DLS) technology is a powerful approach for measuring ultrafine particle size. The correlation method and photon correlation spectroscopy (PCS) are two methods of DLS technology. However, measurement accuracy of the correlation method and PCS based on traditional power spectrum is lower under the condition of the small amount of measurement data. For measurement problem of the small amount of data, PCS based on auto-regressive (AR) power spectrum is proposed in this paper. According to existing small amount of measurement data, this method can forecast subsequent data by an AR model, and then estimate the power spectrum of the data, which can achieve the measurement accuracy of the large amount of data. Besides, the optimal fast Fourier transform (FFT) points of 50 nm–1000 nm particles are obtained by analyzing the mean square error (MSE) of the AR power spectrum and its theoretical power spectrum in different FFT points. The results of simulation and experiment data demonstrate that the AR power spectrum method might serve as an effective approach to PCS measurement problem with the small amount of data.

1. Introduction

Dynamic light scattering (DLS) technology is an effective approach for measuring ultrafine particle size [1–3] which has been applied in physics, chemistry, medicine, and fluid mechanics for decades [4–7]. Its principle is based on the Brownian motion of the ultrafine particles in the suspension. The random motion of the particles leads to the random fluctuations of the scattered light intensity. The fluctuations relate to the particle size. The correlation method [8,9] and the power spectrum method [10,11] are two methods of DLS technology. The power spectrum method is commonly called photon correlation spectroscopy (PCS). The correlation method obtains the particle size by measuring and inverting the autocorrelation function (ACF) of scattered light intensity signal, while PCS obtains the particle size by measuring and inverting the power spectrum of scattered light signal. In the measurement, the scattering light signal is very weak. The inevitable noises easily affect the measurement accuracy. In order to reduce the effect of the noises, the correlation method and traditional power spectrum method need a large amount of measurement data. In general, the amount of data requires a million points [12,13] which implies a very long measurement time. However, in the actual measurement, the measuring time is always limited, especially in some short-term and fast-measurement instances. In these cases, the measured ACF and power spectrum provide poor accuracy, which will ultimately affect the accuracy of the particle size measurement. For the measurement problem of the small amount of data, the literature [14] suggests a PCS based on a wavelet power spectrum method. The amount of data of this method is reduced to 65,536 points. However, when wavelet transform scale is greater, the computation time of the wavelet transform is long, which also leads to a relatively long measurement time. In view of these causes, this paper puts forward a new method of particle size measurement using small amounts of data and small measurement time. This method measures the particle size by PCS. The estimation of the power spectrum is the key problem in PCS. In the traditional power spectrum method, the data outside of measurement data is regarded as zero. Thus, when the amount of data is very small, the resolution of power spectrum estimation is very poor. In order to overcome the shortcoming of the traditional method, a modern power spectrum estimation based on an AR model is used for PCS. Based on existing measurement data and the AR model, this method can make a reasonable forecast for the data outside of the measurement data. Thus, AR power spectrum estimation has a relatively high quality of spectrum estimation under the condition of the small amount of data. Accordingly, this method can achieve the measurement accuracy of the large amount of data, whose amount of data can be reduced to 2×10^4 points.

2. Measurement principle of PCS

The experiment setup of PCS is shown in Fig. 1. The incident laser beam focused by the lens irradiates to the sample particles in

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http://dx.doi.org/10.1016/j.optcom.2014.03.089
0030-4018/

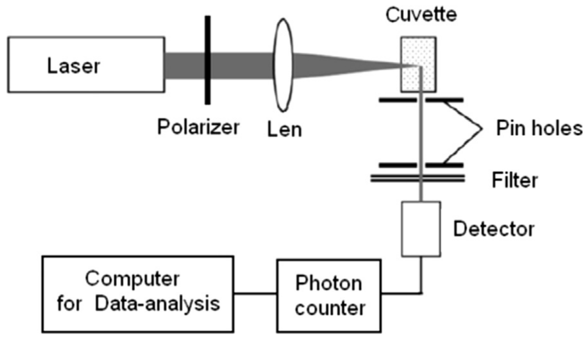

Fig. 1. Experimental setup.

the cuvette. The light scattered by the sample particles first enters into the photodetector through the pin hole and the filter, and is converted into the electrical pulse signal. Then, the pulse signal is counted by the photon counter and input to the computer by USB interface. Finally, we calculate and invert power spectrum of the photon counting signal by the computer, and obtain the particle size. For monodisperse particles, the power spectrum of DLS signal is expressed as the following Lorentzian function:

$$P(\omega)=\frac{2\Gamma/\pi}{\omega^2+(2\Gamma)^2} \tag{1}$$

where ω is the angular frequency and Γ is the decay linewidth which is related to particle size

In Eq. (1), the relation of decay linewidth and the particle size is expressed as

$$\Gamma=Dq^2,\ q=\frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right),\ D=\frac{k_BT}{3\pi\eta d} \tag{2}$$

where d is the diameter of the particles, k_B is the Boltzmann constant, T is absolute temperature, η is the viscosity coefficient, λ is the wavelength of the incident beam in vacuum, n is the refractive index of the dispersion liquid, and θ is scattering angle.

For polydispersity particles, the power spectrum of DLS signal can be expressed as

$$P(\omega)=\sum_{i=1}^{N}G(\Gamma_i)\frac{2\Gamma_i/\pi}{\omega^2+(2\Gamma_i)^2} \tag{3}$$

where Γ_i is the decay rate of the ith kinds of particles, and $G(\Gamma_i)$ is function of decay linewidth depended on the scattering light intensity.

No matter monodisperse particles or polydispersity particles, we only fit the power spectrum of different kind of particles in the computer, and then Γ or Γ_i can be obtained. According to Eq. (2), the different kind of particle sizes can be calculated from Γ or Γ_i.

Similarly, the correlation method obtains the particle size by measuring and inverting the ACF of the photon counting signal in Fig. 1. For monodisperse particles and polydispersity particles, the normalized ACFs of DLS signal are respectively expressed as

$$G(\tau)=\exp(-2\Gamma\tau) \tag{4}$$

$$G(\tau)=\sum_{i=1}^{N}G(\Gamma_i)\exp(-2\Gamma_i\tau)\qquad \sum_{i=1}^{N}G(\Gamma_i)=1 \tag{5}$$

where τ is the sampling time. Considering the parameters of DLS experimental device, Eq. (4) is usually expressed as

$$G(\tau)=\beta\exp(-2\Gamma\tau) \tag{6}$$

where β is a parameter related to experimental conditions. Fitting the ACF, particle size can be obtained.

In this paper, ACFs and power spectrums were fitted by the Levenberg–Marquardt algorithm [15].

3. AR power spectrum estimation

The estimation of the power spectrum is the key in PCS. The principle of AR power spectrum estimation considers that the scattered light signal $I(n)$ is generated by the white noise. The equation generating signal is

$$I(n)=-\sum_{k=1}^{p}a(k)I(n-k)+\omega(n) \tag{7}$$

Eq. (7) is called the AR model, where $I(n)$ is the discrete value of scattered light signal, $\omega(n)$ is the white noise sequence with zero average value and variance δ^2, $a(k)$ $(k=1,2,\ldots,p)$ is the coefficients of the AR model, and p is the model order. Then AR power spectrum estimation is expressed as [16]

$$\hat{P}_I(e^{j\omega})=\frac{\delta^2}{\left|1+\sum_{k=1}^{p}a_ke^{-j\omega k}\right|^2} \tag{8}$$

According to Eq. (8), as long as the parameters of the model δ^2, $a(k)$ and p are determined, the power spectrum $\hat{P}_I(e^{j\omega})$ can be obtained. In other words, the problem of AR power spectrum estimation is essentially the parameters estimation of the AR model. The parameters of the AR model can be solved by the Burg algorithm [17]. Based on minimization principle of the forward and backward prediction errors, the Burg algorithm can get the model parameters. For any p-order model, its forward and backward prediction errors satisfy the following recursive-in-order expression:

$$e_p^f[k]=e_{p-1}^f[k]+k_pe_{p-1}^b[k-1] \tag{9}$$

$$e_p^b[k]=e_{p-1}^b[k-1]+k_pe_{p-1}^f[k] \tag{10}$$

where k_p is the reflection coefficient of the p-order model. Then, the sum of the forward and backward prediction average errors is

$$E_p=\sum_{k=p}^{N-1}\left\{e_p^f[k]^2+e_p^b[k]^2\right\} \tag{11}$$

When E_P takes the minimum value, the reflection coefficient estimation is given by

$$k_p=\frac{-2\sum_{k=p}^{N-1}e_{p-1}^f[k]+e_{p-1}^b[k-1]}{\sum_{k=p}^{N-1}e_{p-1}^f[k]^2+e_{p-1}^b[k-1]^2} \tag{12}$$

According to obtained reflection coefficient, the parameters of the AR model can be solved by the following L–D recursive algorithm [18]:

$$a_p(k)=a_{p-1}(k)+k_pa_{p-1}(p-k)(k=1,2,\ldots,p-1) \tag{13}$$

$$\delta_p^2=\delta_{p-1}^2[1-|k_p|^2] \tag{14}$$

Thus, with Eqs. (12)–(14), δ^2 and $a(k)$ of every order can be solved. However, the Burg algorithm does not give the specific order used for the power spectrum estimation. The usual methods of the AR model order estimation are FPE [19], AIC [20] and MDL [21]; FPE is used in this paper. After the model order and its corresponding parameters are determined, the power spectrum $\hat{P}_I(e^{j\omega})$ can be estimated according to Eq. (8).

4. Numerical simulation and analysis

In order to demonstrate the advantages of the AR power spectrum method, using the correlation method, traditional power spectrum and AR power spectrum method, we preformed the