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The measurement system of nanoparticle size distribution from dynamic light scattering data

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ABSTRACT

The measurement and analysis system of nanoparticle size distribution was developed by using virtual instrument technology, where the photon counting technology was applied in the system to replace the correlator; a high speed photon counter was designed with seamlessly counting technology to reduce the system cost and increase the accuracy. The data of nanoparticle dynamic light scattering (DLS) were analyzed in the mixed program of MATLAB and LabVIEW, where the autocorrelation functions of light scattering signals of 100 nm unimodal as well as 90 nm and 300 nm bimodal particles were inversed by truncated singular value decomposition arithmetic. Experiment results show that the peak position, peak width and symmetry of particle size distributions (PSDs) are very close to the real particles.

1. Introduction

Dynamic light scattering (DLS) technique as a diagnostic tool for particle size distribution (PSD) in solution or colloidal suspensions has been widely used in science and industry [1,2], and the photon correlation spectroscopy (PCS) was used in DLS traditionally, where a digital correlator was used to calculate the autocorrelation function (ACF) and deduce the particle size information. The digital correlator usually costs twice as much as the photon counter. So the paper uses photon counter to distinguish photoelectron pulse from the output of the photomultiplier tube (PMT). This can improve the sensitivity of weak light detection, leave out the correlator and save the cost of the measurement system.

Nowadays, the solution of the PSD from the autocorrelation intensity function needs to inverse the Fredholm integral equations of the first kind, and this has always been a very difficult thing. Many inversion approaches have been proposed such as the Cumulants method [3], Constrained Regularization method (CONTIN) [4], Non-Negative Least Squares method (NNLS) [5], and Tikhonov regularization method [6]. However, these methods are sensitive to noise, as the light scattering signal is very weak, the noise is inevitable [7]; this problem limits their application. To solve the problem, we put forward an inversion method based on truncated singular value decomposition (TSVD) and applied it to the simulated and experimental data inversion.

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2. Hardware design of the system

2.1. The hardware of the system

The hardware of the system is shown in Fig. 1. It consists of a He–Ne laser with a wavelength of 632.8 nm, polarizer, pinholes, convergent lens, cuvette, PMT, photon counter and computer. The PMT is H6240-01of Hamamatsu with standard TTL pulse output, and spectrum responses from 185 nm to 850 nm. A high speed photon counter developed by us was applied to the sample and store the pulses of PMT output. According to light scattering signals, the diameter of the particle is analyzed by the computer. The software platform is LabVIEW 8.0.

2.2. The design of high speed photon counter

The photon counter counts the light pulse signals from the output of PMT at a specific time interval. Schematic diagram of photon counter is shown in Fig. 2. It consists of counting module, clear module, latch module and control module. The obtained low-light signal was sent to amplifier, discriminator and pulse shaping circuit, and the standard photon pulse signal is generated; this signal is a TTL pulse voltage with pulse width of less than 10 ns at minimal. Subsequently, the photon counter counts the photon pulse signals of standard width. The maximum count frequency of photon counter is influenced by the time response characteristics of PMT and the frequency characteristics of weak signal extraction and detection circuit; it is also restricted by the pulse width of standard photon pulse. When the photon pulse width is 10 ns, in order to avoid counter

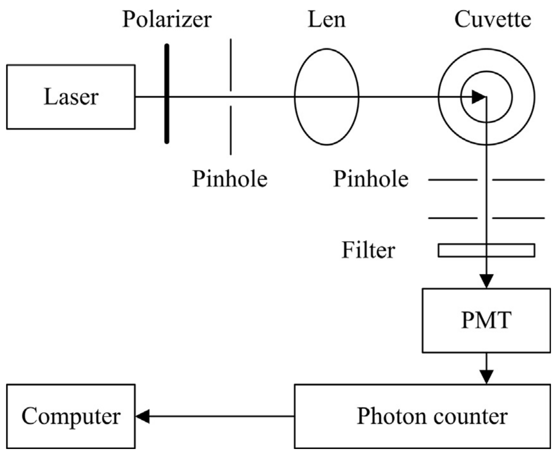

Fig. 1. The hardware of the system.

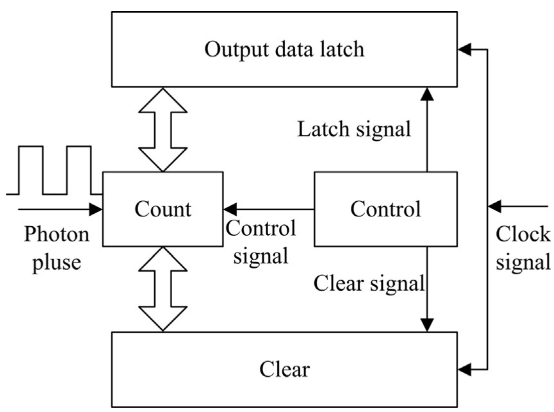

Fig. 2. Schematic diagram of photon counter.

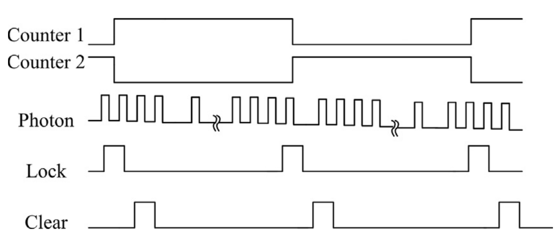

Fig. 3. The control sequence of photon counters.

overflow, a floating-point counter with capacity of 1038 was adopted in the FPGA, so it can meet long time count requirements.

2.3. *The seamlessly counting technology of photon counter*

The photon counter needs to collect all real-time photon pulses, and to work all the time. Because counter stops counting in the latch and clears time period, this will lead to the photon count error. To avoid this count error, two counters are used in the photon pulse counting module, so as to fulfill seamless count. The control sequence is shown in Fig. 3.

By using double counting modules, counting control signals 1 and 2 are complementary, and the two counters of counting modules are controlled by these counting control signals 1 and 2. At the control signal's rising edge, the corresponding counter starts counting. For example, at the falling edge of control signal 1, counter 1 will stop counting, and at the same time, data is latched. After two reference clocks, the latch becomes steady, and then counter 1 is cleared. At the falling edge of control signal 1, the rising edge of the control signal 2 arrives, and counter 2 starts counting. When counter 2 stops counting and is latched and cleared, counter 1 will start to recount. So, by alternating the two counters we can effectively avoid count errors and losses of photon pulse.

3. Measurement algorithm of nanoparticle size

3.1. *Measurement of nanoparticle size*

The laser beam is focalized to the lens and then shot at the particle sample of the sample cell. The scattering light of the particle meets with the photodetector. Scattering light intensity is expressed as follows:

$$I_S = I_S(1)\left[N + 2\sum_{j>i=1}^{N} \cos(\delta_i - \delta_j)\right] \tag{1}$$

where $I_s(1)$ is the scattered intensity of single particle; N is the number of particles in the scattering volume; δ_i and δ_j are phase angles of the electric field of scattered light due to particles i and j, respectively. The autocorrelation function is defined for a signal $I(t)$ as

$$G^{(2)}(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T I(t)I(t+\tau)dt \tag{2}$$

Here $I(t)$ and $I(t+\tau)$ are intensity of the scattered light at t and $t+\tau$ and τ is the delay time.

Normalized intensity autocorrelation function is $g^{(2)}(\tau) = ((G^{(2)}(\tau))/(\langle I(t)\rangle)^2)$. For a Gaussian light field, the normalized electric field autocorrelation function and the normalized light intensity autocorrelation function meet the Siegert relation:

$$g^{(2)}(\tau) = B + \beta[g^{(1)}(\tau)]^2 \tag{3}$$

where $g^{(1)}(\tau)$ is the normalized autocorrelation function of the electric field, B is the experimental baseline, and β is the degree of coherence of light scattering:

$$g^{(1)}(\tau) = \frac{\langle E_s(t)E_s^*(t+\tau)\rangle}{\langle E(t)\rangle^2} \tag{4}$$

where $E_s(t)$ and $E_s^*(t+\tau)$ are scattering electric field strength at t and $t+\tau$. If the sample is monodisperse, normalized autocorrelation function of the electric field can be given by

$$g^{(1)}(\tau) = \exp(-\Gamma\tau) \tag{5}$$

where Γ is the characteristic decay constant

$$\Gamma = q^2 D \tag{6}$$

Here q denotes the scattering vector, D is the diffusion constant, according to the Stoes–Einstein relation

$$D = \frac{K_B T}{3\pi\eta d} \tag{7}$$

where K_B is Boltzmann's constant, T the temperature, and η the viscosity. The particle size can be determined, if the sample is monodisperse.

In the case of the polydisperse sample, normalized autocorrelation function of the electric field is given by

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma)\exp(-\Gamma\tau)d\Gamma \tag{8}$$

where $G(\Gamma)$ is the distributing function of normalized decay width:

$$\int_0^\infty G(\Gamma)d\Gamma = 1 \tag{9}$$

The particle size distributions can be computed if we inverse $G(\Gamma)$ from Eq. (8), by means of the TSVD algorithm.