Size measurement of nano-particles using self-mixing effect

Huarui Wang (王华睿)[1,2] and Jianqi Shen (沈建琪)[1]

[1] *University of Shanghai for Science and Technology, Shanghai 200093*

[2] *Xuzhou Normal University, Xuzhou 221116*

Received February 27, 2008

In this letter, the technique of laser self-mixing effect is employed for nano-particle size analysis. In contrast to the photon correlation spectroscopy (PCS) and photon cross correlation spectroscopy (PCCS), the main advantages of this technique are sensitive, compact, low-cost, and simple experimental setup etc. An improved Kaczmarz projection method is developed in the inversion problem to extract the particle size distribution. The experimental results prove that nano-particle size can be measured reasonably by using the self-mixing effect technique combined with the improved projection algorithm.

OCIS codes: 290.5820, 290.5850, 290.1350, 290.3700.

doi: 10.3788/COL20080611.0871.

The characteristics of many modern materials are often determined by the properties of nano-particle, especially the size of the particle. This fact is responsible for the fast-growing demand for analysis on the nano-particle size. Different kinds of techniques for nano-particle analysis appear in succession. Among them, the well-known techniques are photon correlation spectroscopy (PCS) and photon cross correlation spectroscopy (PCCS)[1]. However, in the PCS and PCCS measurements, the alignment is necessary where the laser and the detector are placed at different locations, which suffers from the complexity of preparation work before measurement. In addition, in the PCS and PCCS principles, the correlation function of the signal is analyzed by the expensive correlator, which leads to a rather high production cost.

Recently, the self-mixing effect technique is introduced into the nano-particle size analysis[2,3]. The self-mixing effect is an optical phenomenon observed when light emitted from a laser cavity reflects off an object and re-enters the laser cavity after an external round trip time. According to the apparatus shown in Fig. 1 in which the laser diode and photodiode are integrated, the self-mixing effect technique is very convenient to align. Besides, it can avoid using the expensive correlator. The power spectrum is got through fast-Fourier transform (FFT) instead and is analyzed for the restoration of particle size. Therefore, the main advantage of this technique is that it offers a sensitive, compact, low-cost, and simple experimental setup and hence it is very hopeful for online applications. However, similar to the PCS and PCCS techniques, the inverse problem in this technique is ill-posed. Small errors in the measurement may give rise to large spurious oscillations in the solution. In this letter, the nano-particle size measurement based on the self-mixing effect is studied with a combination of an improved projection method in the data processing.

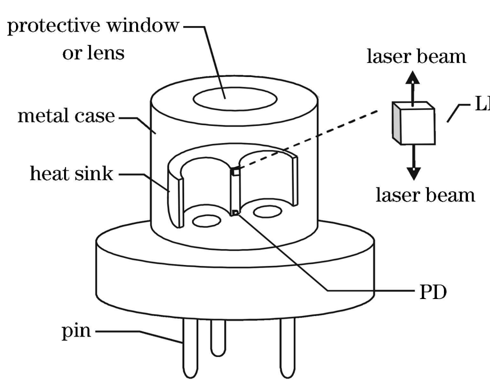

Fig. 1. Laser configuration.

The principle of particle size measurement using self-mixing effect is that the light emitting from the laser hits nano-particles with the Brownian motion and is scattered back into the laser cavity. This causes the periodic change of laser light output frequency, linewidth, threshold gain, and output power, all of which relate to the phase of the backscattering light. The standard internal monitoring photodiode, which is built into the commercial laser diode (LD) package, can be utilized to detect the output signal and to observe the output linewidth. The linewidth of the output power spectrum is related closely to the particle size. Due to their higher average velocity, small particles cause a greater spectrum broadening than large particles do. The intensity spectrum of self-mixing effect follows from the Lorentz function[2−4]:

$$I(\omega) = 2\alpha^2\pi^{-1}n_{\mathrm{p}}\frac{\kappa^2 D(x)}{\omega^2 + [\kappa^2 D(x)]^2}, \quad (1)$$

$$\kappa(\theta) = \left(\frac{4\pi n}{\lambda}\right)\sin\left(\frac{\theta}{2}\right), \quad (2)$$

$$D(x) = \frac{k_{\mathrm{B}}T}{3\pi\eta x}, \quad (3)$$

where α is the polarizability of particle, n_{p} is the average number of particles in scattering volume, ω is the angular frequency, κ is the magnitude of the scattered wave vector, n is the refractive index of the liquid medium, $D(x)$ is the self-diffusion coefficient, θ is the scattering angle ($\theta = \pi$ in the self-mixing effect technique), $k_{\mathrm{B}}T$ is the Boltzmann factor, x is the particle diameter, and η is the viscosity of the solvent.

Despite the advantages of self-mixing effect technique, in restoring the particle size distribution (PSD), it has a main trouble in solving a severe ill-posed linear equation:

$$I_i(\omega_i) = \sum_{j=1}^{N} \underbrace{\bar{x}_j^{-k} \frac{\kappa^2 D_j(\bar{x}_j)}{\omega_i^2 + [\kappa^2 D_j(\bar{x}_j)]^2}}_{A_{ij}} \cdot \underbrace{q_k(\bar{x}_j)\Delta x_j}_{X_j}$$

$$(i = 1, 2, \cdots, M) \quad (4)$$

or in the matrix form:

$$\mathbf{I} = \mathbf{A}\mathbf{X}, \quad (5)$$

where ω_i is the frequency shift in the ith fraction, $\bar{x}_j$ is the average particle diameter in the jth fraction, Δx_j is the corresponding width of the particle size fraction. $\mathbf{A}$ is a matrix which can be obtained theoretically, $\mathbf{I} = (I_1, I_2, \cdots, I_M)^{\mathrm{T}}$ is the intensity of self-mixing effect which can be measured, $\mathbf{X} = (X_1, X_2, \cdots, X_N)^{\mathrm{T}}$ is the PSD to be found. The subscript k of the quantity $q_k(x)$ denotes the dimension of the particle distribution. $q_0(x)$ is the density distribution of particle number, $q_1(x) = xq_0(x)$ is the density distribution of the characteristic line, $q_2(x) = \pi x^2 q_0(x)/4$ is that of the projected area and $q_3(x) = \pi x^3 q_0(x)/6$ is that of the particle volume.

The inverse problem is ill-posed in which even arbitrarily small error components in the measured quantities may give rise to large spurious oscillations in the solution. A number of methods have been developed over the past few years to tackle the inversion problem[5−10]. One of the well-known non-modal inversion algorithms used in particle sizing is the iterative method, for example, the Kaczmarz projection algorithm[11].

In the projection algorithm, the PSD $\mathbf{X} = (X_1, X_2, \cdots, X_N)^{\mathrm{T}}$ is taken as a point in the N-dimensional space and $I_i = \sum_{j=1}^{N} A_{ij} X_j$ is taken as a hyperplane. If there are no experimental errors, the solution is the intersection point of these hyperplanes. The original Kaczmarz projection algorithm is schematically illustrated in Fig. 2(a). The procedure starts from an arbitrary point (i.e., an initial guess) $\mathbf{X}^{(0)} = \left(X_1^{(0)}, X_2^{(0)}, \cdots, X_N^{(0)}\right)^{\mathrm{T}}$. Then, the point is projected onto the hyperplanes one by one in turn and the solution is gradually improved. As the point $\mathbf{X}^{(1)}$ is obtained on the M^{th} hyperplane, the first cycle of iteration is finished and the next cycle of iteration follows. The cycle of iteration is stopped while the found point is sufficiently close to the intersection, i.e., the residual of the measurement reaches a certain threshold.

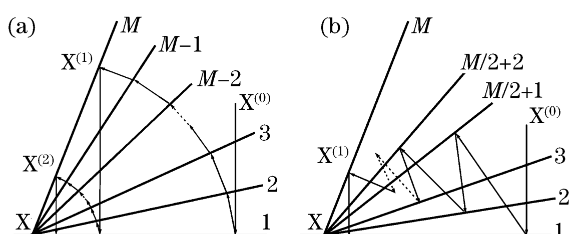

Fig. 2. Schematic illustration of (a) the original Kaczmarz projection algorithm and (b) the improved one.

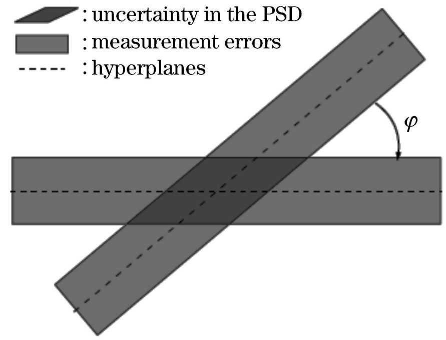

Fig. 3. Effect of measurement errors on the uncertainty in the PSD.

Unfortunately, measurement errors may cause an uncertainty in the solution $\mathbf{X}$. As it is schematically shown in Fig. 3, the errors in the measurements shift the corresponding hyperplanes, which forms the shaded regions around the plane and hence the darker area around the intersection. The darker area denotes the extent of the PSD uncertainty and its size depends on the measurement errors and the skewness between the hyperplanes. If the hyperplanes are badly skewed (i.e., the angle between the planes φ is far away from $\pi/2$), the same amount of measurement error will lead to a large solution uncertainty.

Based on the discussion above, the improvement can be made on the Kaczmarz projection algorithm in which each projection is executed between the little skew hyperplanes. The improved projection method is shown in Fig. 2(b). The guess point is successively projected onto the 1st plane, $(M/2+1)^{\mathrm{th}}$ plane, the 2nd plane, the $(M/2+2)^{\mathrm{th}}$ plane, and so on. Finally, the point is projected onto the M^{th} plane and is finally projected onto the 1st plane again. Then the next cycle follows. Comparing the improved projection algorithm with the original ones, we find that the improved algorithm is able to converge faster and the result is less sensitive to the measurement errors.

Another improvement in the inverse problem is about the PSD used in the algorithm. The PSD of characteristic line ($k = 1$) is chosen because the corresponding matrix element distribution is found to be the most advantageous to restore the PSD among those of four kind PSDs (i.e., $k = 0, 1, 2, 3$). Besides, the smoothness constraint is imposed so as to avoid the oscillations in the restored PSD and the non-negativity constraint is used to preserve the physical meaning of the solution[12]. In this work, the number of size fractions N equals that of the frequency fractions M ($M = N = 50$). Both the particle size fractions and frequency fractions are uniformly distributed on logarithmic scales. The number of the projection cycles is 1000.

The experimental setup configuration is shown schematically in Fig. 4. The wavelength of the laser is 690 nm. The maximum output power of the semiconductor LD is 35 mW, its threshold current is 45 mA and its maximum operating current is 90 mA. In our measurements, the operating current is about 60 mA. The laser is collimated and then focused onto the target. The intensity of the laser is monitored via the current flowing through the photodiode (PD) detector in the semiconductor

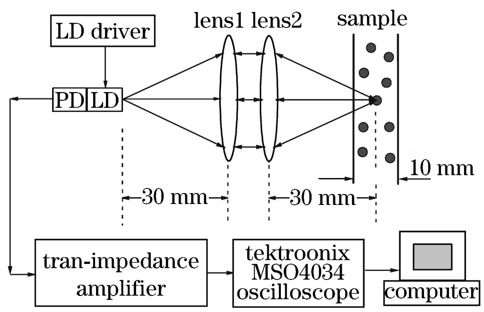

Fig. 4. Experimental setup with the self-mixing effect technique.

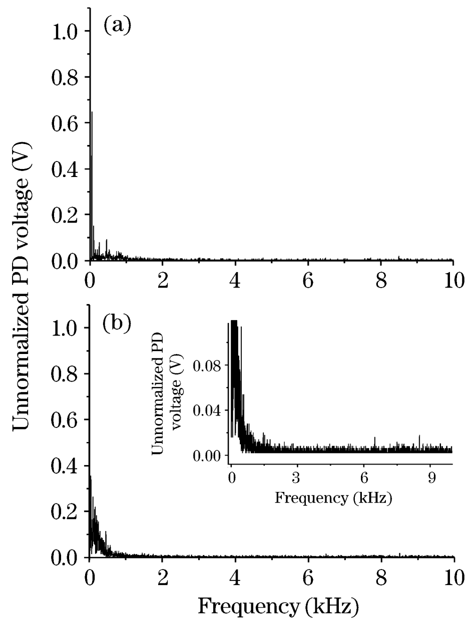

Fig. 5. Measured PD voltage spectrum for 180-nm SiO_2 spheres. (a) Without SiO_2 spheres; (b) with SiO_2 spheres.

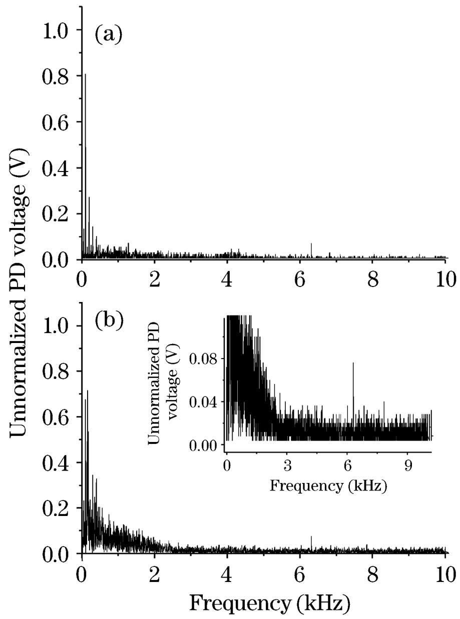

Fig. 6. Measured PD voltage spectrum for 60-nm polystyrene spheres. (a) Without polystyrene spheres; (b) with polystyrene spheres.

package. The current is converted into a voltage signal by a trans-impedance preamplifier connected to a FFT oscilloscope. The signal processing algorithm consists of capturing the FFT from the oscilloscope, a suitable fitting of the intensity spectrum, and restoring of PSD.

The measurements are performed with standard spheres dispersed in the distilled water. The mean particle diameter is 180 nm for SiO_2 spheres and is 60 nm for polystyrene spheres by label. The volume concentration is controlled below 0.5% and the temperature is 293 K. Figures 5 and 6 show the intensity power spectra of the laser measured on the samples. The measurements in absence of spheres are used as a reference. Figure 7 shows the normalized spectra, corresponding to Fig. 5(b) ($x = 180$ nm) and Fig. 6(b) ($x = 60$ nm). The gray areas correspond to the experimental datum and the solid

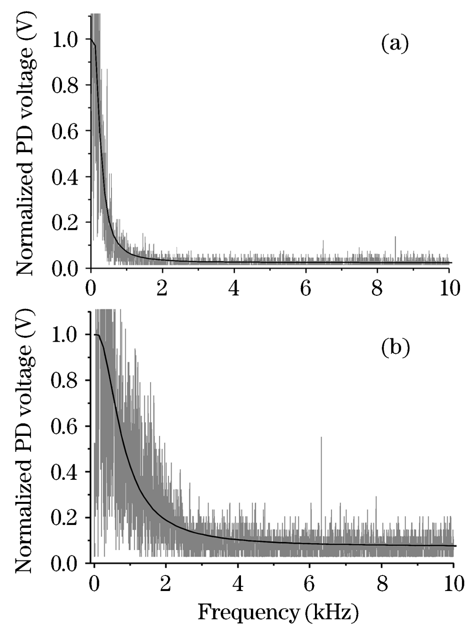

Fig. 7. Normalized spectra. (a) 180 nm; (b) 60 nm.

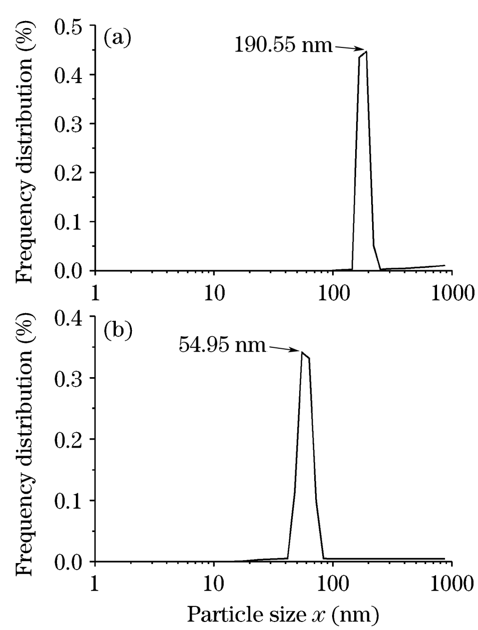

Fig. 8. PSD obtained with the improved projection algorithm. (a) 180 nm; (b) 60 nm.

curves are the fitted Lorentzian functions. It can be seen that smaller particles cause a greater broadening of spectrum than the bigger particles do.

Figure 8 shows the PSD obtained with the improved projection algorithm. It can be found that the results of restoration are relatively consistent with the labeled ones. However, there is a visible spurious distribution in the large particle size range, which is produced by the noises in low-frequency range (as shown in Figs. 5(a) and 6(a)).

In this work, the self-mixing effect technique is used for size measurement of nano-particles. The theory and experimental setup is introduced. The Kaczmarz projection algorithm is improved to reconstruct the PSD, in which each projection is executed between the little skew hyperplanes and the PSD of the characteristic line is chosen for restoration ($k = 1$). The experimental results prove that nano-particle size can be measured reasonably by using the self-mixing effect technique and the improved projection algorithm for the PSD extraction.

This work was supported by the Nano-Project of Shanghai Science and Technology Commission under Grant No. 0452nm029. J. Shen is the author to whom the correspondence should be addressed, his e-mail address is shenjq@online.sh.cn. H. Wang's e-mail address is wanghuar@126.com.

References

1. W. Lämmle, LabPlus International **2,** 19 (2005).
2. C. Zakian, M. Dickinson, and T. King, Appl. Opt. **45,** 2240 (2006).
3. C. Zakian, M. Dickinson, and T. King, J. Opt. A **7,** S445 (2005).
4. B. J. Berne and R. Pecora, *Dynamic Light Scattering with Applications to Chemistry, Biology, and Physics* (Wiley-Intersceince Press, New York, 1976) p.60.
5. B. Ge, J. Wang, Y. Zhang, and H. Li, Chinese J. Lasers **B7,** 430 (1998).
6. M. Kandlikar and G. Ramachandran, J. Aerosol Sci. **30,** 413 (1999).
7. F. Xu, X. Cai, M. Su, Z. Zhao, and J. Li, Chinese J. Lasers (in Chinese) **31,** 223 (2004).
8. J. Worlitschek, T. Hocker, and M. Mazzotti, Part. Part. Syst. Char. **22,** 81 (2005).
9. F. Pedocchi and M. H. García, Appl. Opt. **45,** 3620 (2006).
10. H. Tang, X. Sun, and G. Yuan, Chin. Opt. Lett. **5,** 31 (2007).
11. S. Kaczmarz, Bulletin de l'Académie Polonaise des Sciences et Lettres **A35,** 335 (1937).
12. J. Shen, B. Yu, H. Wang, H. Yu, and Y. Wei, Appl. Opt. **47,** 1718 (2008).