Determination of Particle Size Distribution by the Analysis of Intensity-Constrained Multi-Angle Photon Correlation Spectroscopic Data

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Abstract

Laser light scattering (LLS), especially dynamic laser light scattering (DLS), also known as photon correlation spectroscopy (PCS), is a well established method for particle size distribution analysis. It usually involves a Laplace inversion of the field autocorrelation function. However, the resolution is limited because of the ill-conditioned nature of this Laplace inversion. No unique solution exists when noise is present on the data. In contrast with this ill-conditioned nature, the angular dependence of scattered (static) intensities is precisely not ill-conditioned, which allows the resolution of the ill-conditioned inversion of DLS data to be improved. In order to characterize samples with more complicated size distributions, an intensity-constrained multi-angle PCS data analysis program has been developed, which is an alternative way of normalizing the field correlation function to that reported by *Cummins* and *Staples* [12]. In this program, the field autocorrelation function is normalized to the scattering intensity by using a predetermined coherent factor at each angle, which provides an additional constraint on the Laplace inversion of multi-angle PCS data analysis. The alternative analysis improves the resolution of PCS and provides a more reliable particle size distribution than single-angle data analysis. Both simulated and measured LLS data are used to illustrate its application, resolution and limitations.

1 Introduction

Laser light scattering (LLS, including both static and dynamic light scattering), especially dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS) or as quasi-elastic light scattering (QELS), is a well established method for particle size distribution analysis. In particular, the method is widely used to characterize the particle size distribution in the submicrometre range and to monitor association and dissociation processes, such as aggregation, microemulsion and crystallization processes.

Dynamic light scattering data analysis usually involves a Laplace inversion of the field autocorrelation function. The development of the Laplace inversion analysis for particle size distributions from DLS data has become an active area of research in the last 20 years. Various analysis procedures [1-11], such as cumulants, bimodal, non-negative non-linear least-squares, histograms and exponential sampling, have been developed. Many of them have been used successfully to characterize polymer and colloid systems in terms of molecular weight distribution or particle size distribution.

However, the resolution is limited because of the ill-conditioned nature of this Laplace inversion. No unique solution exists when noise is present on the data. Two regularization methods, maximum entropy [9] and minimum of curvature (as in the CONTIN program [3]), have mostly been used to approach this problem. In contrast to this ill-conditioned nature, the angular dependence of scattered (static) intensities is precisely not ill-conditioned, which allows the resolution of the ill-conditioned inversion of dynamic light scattering data to be improved. In the past, much effort have been spent on the development of an analysis procedure that can produce a more constrained and less arbitrary solution.

Recently, the analysis of multi-angle photon correlation spectra has attracted some attention [12]. This analysis puts both intensities and photon correlation functions at two or more scattering angles into the Laplace inversion, wherein the intensity scattered by each species is normalized by the intensity scattered by the same species at a particular angle. This additional information supplied by the scattered intensities at different scattering angles provides a very severe constraint on the range of possible solutions. A resolution can be achieved that is unobtainable by using a single-angle data analysis.

In order to characterize samples with more complicated size distributions, such as bimodal or even trimodal, an intensity-constrained multi-angle photon correlation spectroscopic data analysis program based on the above multi-angle analysis principle has been developed to characterize particle size distributions, wherein the intercept of the field correlation function is normalized to the intensity obtained from static light scattering by using the predetermined coherent factor so that the calculated correlation function at each angle is proportional to the measured one with an identical proportional constant for all scattering angles, which is an alternative way of normalizing the field correlation function to that reported by *Cummins* and *Staples* [12].

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This program has been tested with both simulated photon correlation functions and mixtures of narrowly distributed standard latex samples. In this paper, in addition to illustrating its basic principles, we use several tested examples to discuss the application, resolution and limitations of the program.

2 Basic Principle

From a photon correlation spectrometer, an intensity-intensity autocorrelation function ($G^{(2)}(n\Delta\tau, \theta) = \langle I(0, \theta) \cdot I^*(n\Delta\tau, \theta)\rangle$) is measured. Following the assumptions that the optical field possesses Gaussian statistics, the measured autocorrelation function can be assumed to characterize purely diffusive processes. Therefore, the following relationship is valid:

$$G^{(2)}(n\Delta\tau, \theta) = A\,[1 + \beta(\theta)\,|g^{(1)}(n\Delta\tau, \theta)|^2] \quad (1)$$

where A, $g^{(1)}(n\Delta\tau, \theta)[\equiv \langle E(0, \theta) \cdot E^*(n\Delta\tau, \theta)\rangle]$, θ, $\Delta\tau$ and $\beta(\theta)$ are the measured baseline, the normalized field autocorrelation function, the scattering angle, sample time and the coherent factor depending only on the optical design of the instrument, respectively. It should be pointed out that $n(1 \le n \le M)$ represents the channel number, where M is the total channel number of the correlator. However, for a general case, it is not necessary to have n as an integral number, i.e. $n\Delta\tau$ should be written as delay time, t. For a polydisperse system, $g^{(1)}(n\Delta\tau, \theta)$ takes the form

$$g^{(1)}(n\Delta\tau, \theta) = \int_0^\infty G(\Gamma(\theta))\, e^{-\Gamma(\theta) n\Delta\tau}\, d\Gamma \quad (2)$$

where $G(\Gamma(\theta))$ represents the line-width (Γ) distribution. If the particles are isotropic and non-interacting and number-density fluctuations are insignificant, Γ can be related to the translational diffusion coefficient, D, through $\Gamma = DK^2$, where K (scattering vector) $= 4\pi n_s[\sin(\theta/2)]/\lambda$ and n_s, θ and λ are the solvent refractive index, the scattering angle and wavelength, respectively. D can be further related to the particle diameter, d, by using the well known Stokes-Einstein equation: $d = k_B T/(3\pi\eta D)$. The line-width distribution can be converted, for homogeneous spherical particles, into the particle number distribution, $N(d)$, by the application of appropriate Mie coefficients [13]:

$$G(\Gamma(\theta))\, d\Gamma = N(d) \cdot i(\theta, d, n_p)\, dr \quad (3)$$

where n_p and $i(\theta, d, n_p)$ are the refractive index of the particle and the scattered light intensity at angle θ, respectively. $i(\theta, d, n_p)$ can be calculated according to the Mie theory [13] for a homogeneous sphere with a given set of θ, d and n_p.

The Laplace inversion of the measured $\beta\,|g^{(1)}(n\Delta\tau, \theta)|$ to $N(d)$ belongs to a class of ill-conditioned problem. No unique solution exists because noise is always present on the measured data. The validity of $G(\Gamma)$ or $N(d)$ by using such a transformation is dependent on both noise in the measured correlation functions and scattering intensities. Therefore, the calculated $G(\Gamma)$ or $N(d)$ has to be justified in terms of the real particle size distribution, not only in terms of the fitting quality. In principle, with more additional information to constrain the analysis, the resulting distribution would be more reliable. Unfortunately, most of the time, there is no additional information available about the particle size distribution of a measured sample.

In practice, the measured $G^{(2)}(n\Delta\tau, \theta)$ is "normalized" by either a calculated or a measured baseline, i.e. $\langle I(\theta)\rangle^2$ or A, respectively, which implicitly assumes that the optical field possesses Gaussian statistics. Normally, the normalized correlation function, $C(n\Delta\tau, \theta)$, is in the form

$$C(n\Delta\tau, \theta) = \beta(\theta)\,|g^{(1)}(n\Delta\tau, \theta)|^2 = [G^{(2)}(n\Delta\tau, \theta) - A]/A\ . \quad (4)$$

Figure 1 shows a typical measured "normalized" $C(n\Delta\tau, \theta)$ of a latex dispersion, which is a mixture of three narrowly distributed latexes where the diameters (volume ratios) are 90 nm (70%), 312 nm (20%) and 490 nm (10%). As seen in Figure 1, the intercept of $C(n\Delta\tau, \theta)$ at $t \to 0$ (or $n = 0$) is not 1, but ~0.4.

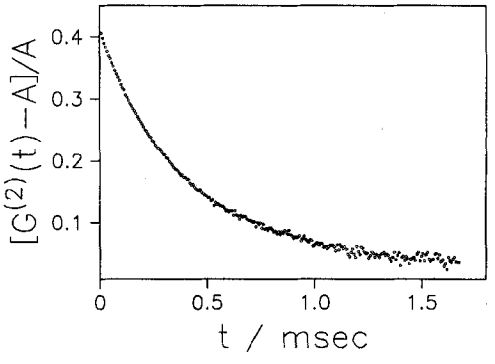

Fig. 1: Typical measured "normalized" intensity-intensity time correlation function $C(n\Delta\tau, \theta)$ of a latex dispersion, which is a mixture of three narrowly distributed latexes ($d_1 = 90$ nm, $d_2 = 312$ nm, $d_3 = 490$ nm with a volume ratio of $V(d_1):V(d_2):V(d_3) = 7:2:1$).

In our instrument, an intercept of 0.8 can be reached. However, in order to compromise both static and dynamic light scattering we chose a relatively larger pinhole, which is why the intercept is around 0.4. This value is typical for a laser light scattering spectrometer which is designed for both static and dynamic LLS measurements without changing the optical set-up. $C(n\Delta\tau, \theta)$ collected at different scattering angles will have different intercepts $\beta(\theta)$ when $t \to 0$ (or $n = 0$) and different "residual" baselines when t (or n) $\to \infty$. To our knowledge, the intercept is taken as a fitting parameter in all single-angle dynamic light scattering data analysis programs, such as cumulants, bimodal, nonnegative non-linear least-squares, histograms, exponential sampling, CONTIN and MSVD (single-value decomposition) [1-11]. It is well known that for a broadly distributed sample the value of the intercept is not a very well defined parameter. For example, it depends on the ratio of the sample time to the average relaxation time. However, in contrast, the coherent factor $\beta(\theta)$ depends only on the optical arrangement of a given LLS spectrometer. Theoretically, only for a monodisperse sample, the intercept equals $\beta(\theta)$. Therefore, in practice, by measuring $C(n\Delta\tau, \theta)$ of a very narrowly distributed latex sample and extrapolating such a measured $C(n\Delta\tau, \theta)$ to $n = 0$, i.e. $C(0, \theta)$, we are able to determine $\beta(\theta)$ at each scattering angle θ and use these values later to normalize the measured $C(n\Delta\tau, \theta)$. In such a way, we can fix one fitting parameter experimentally, which constrains our data analysis.

If we are only considering a single angle, this normalization obviously removes any explicit information regarding the intensity variation with scattering angle. However, when two or more angles are involved, the relative intensity change should be preserved after the normalization. In order to constrain the Laplace inversion of Eq. (2) with as much of the measured information as possible, the following multi-angle analysis principle is applied. If the LLS experiment is carried out at several scattering angles ($\theta_1, \theta_2, \ldots, \theta_p$), our object is to find a proper

particle size distribution ($N(d)$) satisfying the following equation:

$$\sum_{j=1}^{p}\sum_{n=0}^{M}\langle I(\theta_j)\rangle\left[\frac{C(n\Delta\tau,\theta_j)}{\beta(\theta_j)}\right]^{1/2} = \sum_{j=1}^{p}\sum_{n=0}^{M}\int_0^{\infty} i(\theta_j, d, n_p)\,N(d)\,e^{-\Gamma(\theta_j)n\Delta\tau}\,dd \quad (5)$$

where $\langle I(\theta_j)\rangle$, $C(n\Delta\tau, \theta_j)$ and $\beta(\theta_j)$ are experimental data and $i(\theta, d, n_p)\,e^{\Gamma(\theta_j)n\Delta\tau}$ for each given set of d, θ_j and n_p can be calculated. It should be emphasized that n (i.e. t) starts from 0 in Eq. (5), which means that not only correlation functions but also the scattered intensities are used in our Laplace inversion. Hence, in principle, our analysis should be more constrained in comparison with the other data analysis methods where $C(0, \theta_j)$ is only a floating parameter. Eq. (5) is discretized by approximating the integral in Eq. (2) with a summation. dd (or more strictly Δd) as a constant can be absorbed into $N(d)$. In logarithmic space, $dd = dd[ln(d)]$. Therefore, $i(\theta_j, d, n_p)$ $\exp(-\Gamma(\theta_j)\,n\Delta\tau)$ has to be multiplied by d. $d[ln(d)]$ (or $\Delta[ln(d)]$) as a constant in logarithmic space can be absorbed in $N(d)$. Eq. (5) can be rewritten in the following matrix form:

$$|Z|_{(M+1)px1} = |Y|_{(M+1)pxk} \cdot |X|_{kx1} \quad (6)$$

where $|Z|\,[=\langle I(\theta_j)\rangle\left[\frac{C(n\Delta\tau,\theta_j)}{\beta(\theta_j)}\right]^{1/2}$, $n = 0$ to M; $j = 1$ to p] and $|X|\,[= N(d_j)$, $j = 1$ to k] are vectors and $|Y| = [i(\theta_j, d_j)\,e^{-\Gamma(\theta_j)n\Delta\tau}$, $n = 0$ to M; $j = 1$ to p] is one matrix with $(m+1)\cdot p \cdot k$ elements. The calculation of $|X|$ is regularized by a second-order derivative operator which penalizes solutions for unwanted, non-physical or unrealistic features. The relative contribution of the regularizer to the data fit can be tuned by choosing different values of a multiplicative constant α, which depends on the noise level in the experimental data [4]. A computer program based on this principle has been developed in our laboratory by using *Hansons*'s least-squares calculation [14] where a non-negativity constraint is used. The program accepts data sets that are either equi- or logarithmic distant in time. The contribution of static and dynamic LLS data can be varied. It has been found that if we use only static LLS data (i.e., the scattering intensity), the result is very sensitive to the refractive index of the particles. In our present program, the initial particle size range was chosen and rejected manually. In principle, the selection of the size range can be done automatically. The program can be installed and run on a typical IBM/PC-AT 486 computer. The typical running time is ~2 min. Here we have omitted the details of the computing program as it is not the key point in this paper. After obtaining $N(d)$, the volume or weight distribution can be calculated by assuming that particles are homogeneous spheres.

In practice, $G^{(2)}(n\Delta\tau, \theta)$ and $I(\theta)$ are typically measured at 6–10 scattering angles ranging from 30° to 140°. In general, for a broadly distributed sample with a diameter comparable to the laser wavelength, $G^{(2)}(n\Delta\tau, \theta)$ and $I(\theta)$ at more scattering angles are measured and used in the data analysis.

3 Applications and Discussion

3.1 Simulated Data

Based on a number distribution function

$$N(d) = \frac{\delta(d-d_1)}{d_1} + \frac{\delta(d-d_2)}{d_2} \quad (7)$$

time correlation functions and scattered intensities at eight different scattering angles ranging from 30° to 100° without adding artificial noise by choosing $d_1 = 300$ nm, $d_2 = 500$ nm, $n_p = 1.6$, $n_s = 1.33$ and a number ratio $N(d_1):N(d_2) = 1:1$ for a logarithmically discretized size axis. These simulated data were analysed with our intensity-constrained multi-angle photon correlation spectroscopic (ICMPCS) program.

Figure 2 shows six calculated number distributions with different regularization factors α ranging from 10^{-9} to 10^{-4}, where the x- and y-axes are logarithmically and linearly spaced. It can be seen that the results are fairly stable in spite of the change in α and the bimodal distribution is resolved with a number ratio of 1.00:1.04 and two peaks located around the input values. This is expected and understandable because there no artificial noise was added in our simulated data, i.e. our simulated data are "perfect". Therefore, we have to use the real experimental data to verify the program.

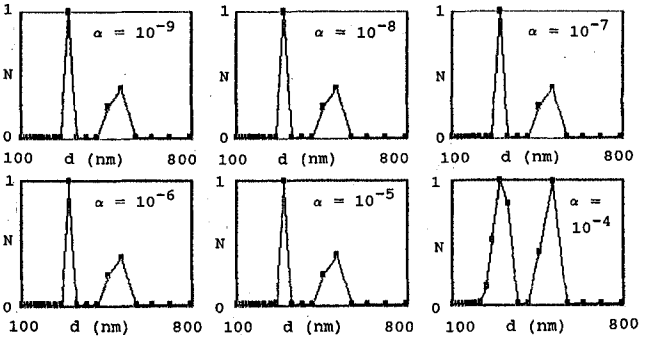

Fig. 2: Calculated number distributions of a simulated bimodal distribution ($d_1 = 300$ nm and $d_2 = 500$ nm with a number ratio of $N(d_1):N(d_2) = 50:50$), where seven scattering angles (20–110°) were used.

3.2 Experimental Data

Two types of latex mixtures were used in LLS experiments. Sample 1 was a mixture of two narrowly distributed latexes ($d_1 = 90$ nm, $d_2 = 312$ nm, $n_p = 1.6$ and a volume ratio of $V(d_1):V(d_2) = 19:1$) and sample 2 was a mixture of three narrowly distributed latexes ($d_1 = 90$ nm, $d_2 = 312$ nm, $d_3 = 490$ nm, $n_p = 1.6$ and $V(d_1):V(d_2):V(d_3) = 7:2:1$), where the uncertainty in the volume ratio was about 10%. The solutions were extremely diluted so that there was just enough intensity (~10000 counts per second) for the measurement.

A commercial LLS spectrometer (ALV/SP-86, Germany) was used. An argon ion laser (Coherent INNOVA 300, operated at 488 nm) was used as the light source. The primary beam was vertically polarized. By placing a polarizer in front of the detector, we measured only the vertically polarized scattered light. An ALV 3000 correlator with 240 linear channels was used to measure the intensity-intensity time correlation functions. All measurements were carried out at 25.0 ± 0.1 °C.

Figure 3 shows six volume distributions of sample 1, which were calculated from the measured LLS data by using our ICMPCS program with different regularization factors α ranging from 10^{-12} to 10^{-7}. As can be seen, this latex mixture has been resolved. The resulting bimodal distributions are fairly stable with two peaks located at ~90 nm and ~310 nm and an expected volume ratio of ~95:5. For comparison, we took the same experimental data as used in Figure 3, but used only one angle each time, to calculate the particle size distribution of this latex mixture.

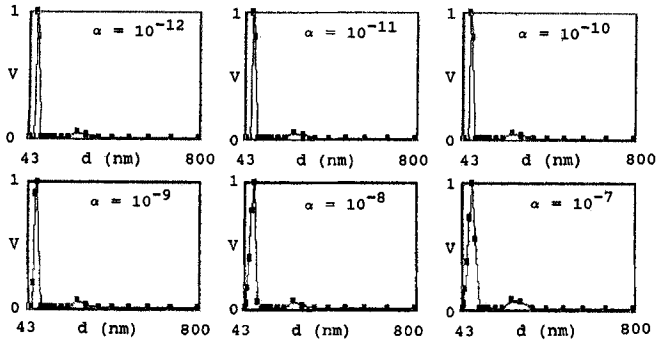

Fig. 3: Calculated volume distributions of a latex dispersion, which is a mixture of two narrowly distributed latexes ($d_1 = 90$ nm and $d_2 = 312$ nm with a volume ratio of $V(d_1):V(d_2) = 95:5$) where 11 angles (40-90°) were used.

Figure 4 shows six particle size distributions calculated for different scattering angles θ. As discussed in the previous section, single-angle data analysis will distort the particle size distribution, which means that either it cannot resolve this bimodal latex mixture or it gives an incorrect volume ratio. The distortions can be clarly seen in Figure 4. In practice, six to nine scattering angles are mostly used in order to obtain an improved and stable particle size distribution. However, there is no general way to predict which combination of scattering angle is best for a given system.

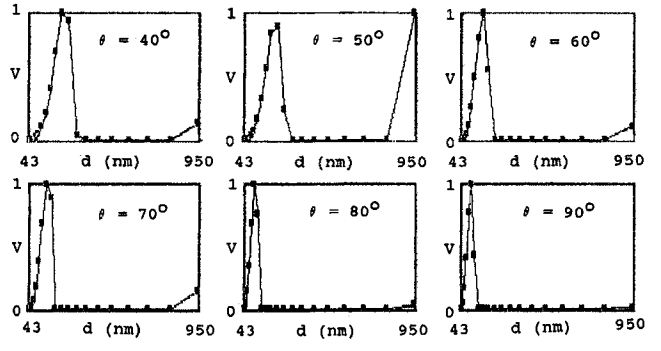

Fig. 4: Calculated volume distributions from the data in Figure 3, where only one scattering angle was used in each calculation.

Figure 5 shows nine volume distributions of sample 2, which were also calculated from the measured LLS data by using our ICMPCS program with different regularization factors α ranging from 10^{-13} to 10^{-5}. As can be seen, the resulting trimodal distributions are fairly stable with three expected peak locations (~90 nm and ~310 nm and ~490 nm) and the expected volume ratio when $\alpha < 10^{-8}$. However, when $\alpha > 10^{-7}$, the resulting distributions are distorted. We also found that a two-angle analysis is unable to resolve this trimodal distribution, whereas a six-angle analysis does.

In practice, there is always some kind of experimental noise in the measured correlation functions and the scattering intensities. The questions that have to be addressed are how we reject only noise, but not information, and which α should be chosen. If α is chosen too low, noise will influence the analysis, resulting in a false particle size distribution. If α is chosen too high, some valuable information will be lost and the real particle size distribution will be distorted, such as when $\alpha > 10^{-7}$ in Figure 5. In order to increase the chance of finding a suitable α, we have applied four different criteria to make a judgement on the solution of $N(d)$. The first is calculated from the regularization (i.e. pure mathematical minimum), the second from the measured and calculated scattering intensities (i.e. the terms of $n = 0$ in Eq. (5)), the third from the measured and calculated intercept and the fourth from the measured and calculated $\beta(\theta)$. To choose the best solution, we weight the four criteria equally and choose an overall minimum of the four criteria in practice. In this way, we look for not only a best fit from the mathematical point of view, but also a best fit from the physical point of view, which is based on the measured scattering intensities, $I(\theta)$, and the experimentally determined coherent factors, $\beta(\theta)$.

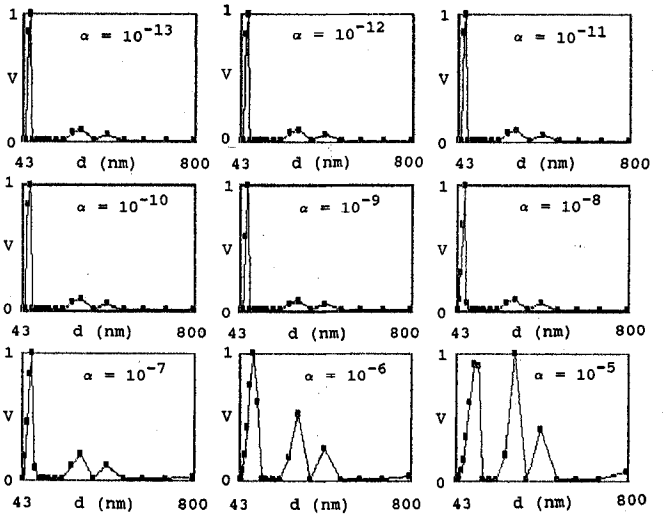

Fig. 5: Calculated volume distributions of a latex dispersion, which is a mixture of three narrowly distributed latexes ($d_1 = 90$ nm, $d_2 = 312$ nm and $d_3 = 490$ nm with a volume ratio of $V(d_1):V(d_2):V(d_3) = 7:2:1$), where six angles (40-90°) were used.

4 Conclusions

A method of analysis of intensity-constrained multi-angle photon correlation spectroscopic data has been developed, which is an alternative way of normalizing the field correlation function to that reported by *Cummins* and *Staples* [12]. The alternative analysis improves the resolution of photon correlation spectroscopy and provides a more reliable particle size distribution than single-angle data analysis. Therefore, LLS as a non-invasive and non-destructive analytical method is now more suitable for characterizing more broadly distributed samples. It has been shown that even trimodal distributions can be resolved as long as those modes are not too closely located and each mode contributes a comparable amount of scattered intensity. When the particle size ratio of the two modes is <2, it will be difficult to determine whether the distribution is monomodal or bimodal, especially if the two modes themselves are broadly distributed. There is no question that, if only in terms of resolution, photon correlation spectroscopy (PCS) will probably never reach the same level as fractionation methods such as ultracentrifugation and chromatography. However, PCS as a supplementary technique has many unique advantages in particle size analysis: it is non-destructive, relatively fast and adaptable for on-line measurements.

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6 Symbols and Abbreviations

d	particle diameter
D	translational diffusion coefficient
DLS	dynamic light scattering
$g^{(1)}(n\Delta\tau,\theta)$	normalized electric field autocorrelation function
$G(\Gamma(\theta))$	line-width distribution at θ
$G^{(2)}(n\Delta\tau,\ \theta)$	intensity-intensity autocorrelation function
$i(\theta,\ d,\ n_p)$	scattered light intensity
ICMPCS	intensity-constraint multi-angle PCS
K	scattering vector
LLS	laser light scattering
n	channel number
n_p	refractive index of particle
n_s	refractive index of solvent
$N(d)$	number distribution
PCS	photon correlation spectroscopy
QELS	quasi-elastic light scattering
$V(d)$	volume distribution
α	regularization factors
$\beta(\theta)$	coherent factor at θ
$\Delta\tau$	sample time
Γ	line-width
η	solvent viscosity
θ	scattering angle
λ_0	incident laser wavelength

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