Estimation of Distribution Functions in Light Scattering: The Regularization Method and Bayes' Ansatz

Ralf Buttgereit, Michael Marth, Josef Honerkamp*

Albert-Ludwigs-Universität, Fakultät für Physik
Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau, Germany

SUMMARY: An important step in the analysis of dynamic light scattering data is the estimation of the correlation time distribution given the measurement of the autocorrelation time function. This is an inverse problem, and especially a so-called ill-posed inverse problem: The map from the correlation time distribution to the autocorrelation time data is singular, a unique inverse of this map does not exist. Such problems are usually treated by regularization methods. By those an estimator for the relaxation time spectrum is defined which differs from the usual Least Squares estimator in conceptual background as well as in numerical effort at its implementation.
We discuss the regularization method from the Bayesian point of view. The choice of the additional prior functional is discussed and also two strategies for the determination of the so-called regularization parameter. After this more general introduction two aspects which are more specific for the light scattering are addressed: The influence of the model for the experimental errors on the quality of the estimation and the generalization of the regularization method to the multi-angle scattering.
The size of the experimental errors and their correlation enter significantly into the mathematical expression for the estimator of the correlation time distribution. They can be calculated either from the autocorrelation function using a model derived by Schätzel, or, on the other hand, they could be computed directly from the time series of the scattered light, if such a time series is stored during the experiment. We show by simulations that the direct method indeed leads to better results than the use of the model by Schätzel, but that already this use leads to an improvement compared to an analysis, in which the correlation of the experimental errors is neglected at all.
The analysis of multi-angle data can easily be incorporated into the framework of regularization methods. At first thought one would combine the estimations of the relaxation time spectrum based on the measurements for the different angles by calculating the mean or some weighted mean of the estimates. We show that this does not lead to the best results, however. The estimation of the relaxation time spectrum from all the multi-angle data at once leads to better results than the intuitive combination.

Introduction

 CCC 1022-1360/00/$ 17.50+.50/0

Scattering of electromagnetic radiation is an expedient tool to study the structure of matter. The distribution and movement of macromolecules dissolved in a liquid can be investigated using radiation with a wavelength in the optical range. In this range the wavelength is larger than the size of the macromolecules and smaller than the distances between them. Two kinds of experimental setups for light scattering have to be distinguished: static light scattering (SLS) which gives information about the particle size distribution of the dissolved macromolecules, and dynamic light scattering (DLS) which is used to investigate their motion.

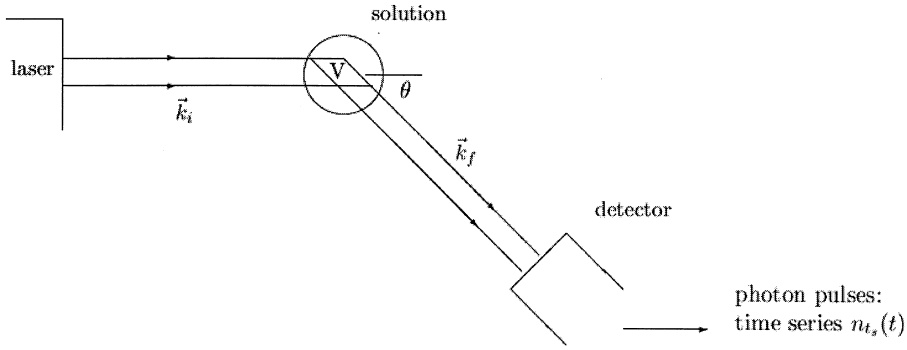

Fig. 1: Schematic illustration of the experimental setup in a DLS experiment.

Fig. 1 shows the basic experimental setup for DLS (see also ref. 1). A laser emits photons with wavelength λ_L. These photons pass through the solution and part of them are scattered by the macromolecules under the angle θ which is the angle between the initial and final wavevector $\mathbf{k}_i$ and $\mathbf{k}_f$. If this scattering process is assumed to be elastic, the length of the scattering vector $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is constant and given by [2]:

$$q = |\mathbf{q}| = 4\pi \frac{n}{\lambda_L} \sin(\theta/2), \tag{1}$$

in which n is the refractive index of the solvent.

If internal degrees of freedom can be neglected a typical time constant characterizing the motion of a macromolecule can be introduced by

$$\alpha = 1/Dq^2, \tag{2}$$

in which D denotes the diffusion constant of this macromolecule. This time constant α (the correlation time) is a characteristic time of the time series of the scattered light. Macromolecules of different size have different correlation times α, and the correlation time

distribution $h_\alpha(\ln\alpha)$ is often used as the spectrum of these different time constants. The determination of $h_\alpha(\ln\alpha)$ is an important step in the analysis of DLS data.

The starting point for the analysis of DLS data is the time series $n_{t_s}(t)$. This time series represents the number of scattered photons arriving at the detector during the sampling time t_s. In a first step this time series is used to estimate the autocorrelation time function $g(\tau)$ which is defined by

$$g(\tau) \equiv \frac{< N_{t_s}(t) N_{t_s}(t+\tau) >}{< N_{t_s} >^2} - 1, \tag{3}$$

where $N_{t_s}(t)$ stands for a random variable with realization $n_{t_s}(t)$. A typical estimator for $g(\tau)$ in terms of these realizations will be given in eq. (24). Typically, such an estimation is performed during the experiment using a hardware correlator such as the ALV 3000 [3] or ALV 5000 [4].

From the autocorrelation time function $g(\tau)$ the correlation time distribution $h_\alpha(\ln\alpha)$ is estimated. If the autocorrelation time function of one scatterer is a decaying exponential then $h_\alpha(\ln\alpha)$ and $g(\tau)$ are related by [5]

$$g(\tau) = \beta \left(\int_{-\infty}^{\infty} d\ln\alpha \; e^{-\tau/\alpha} \, h(\ln\alpha) \right)^2 + \varepsilon(\tau), \tag{4}$$

where β denotes the coherence parameter which depends on the experimental setup and ε is the measurement error. The term

$$g_{EE}(\tau) = \int_{-\infty}^{\infty} d\ln\alpha \; e^{-\tau/\alpha} \, h(\ln\alpha), \tag{5}$$

is the autocorrelation time function of the amplitudes of the electric fields of the scattered photons. $g(\tau)$ is the autocorrelation time function of the intensities of the scattered photons.

The correlation time distribution $h_\alpha(\ln\alpha)$ is essentially the product of the relaxation time spectrum of the scatterers $h_D(\ln D)$ and their relative scattering amplitude. $h_\alpha(\ln\alpha)$ is sometimes also denoted as relative amplitude of the decay process.

The estimates of the autocorrelation time function $g(\tau)$ are affected by two kinds of errors. First, the autocorrelation time function $g(\tau)$ itself is affected by the measurement error. Second, because of the finite length of the time series the estimates $\hat{g}(\tau)$ of $g(\tau)$ are affected by correlated statistical errors. Only estimates of the autocorrelation time function are

accessible by experiment. Therefore, any accessible autocorrelation time function in DLS is affected by correlated statistical errors.

Equation (4) constitutes a map between the function $h_\alpha(\ln\alpha)$ and the experimentally accessible function $g(\tau)$. Given the function $h_\alpha(\ln\alpha)$ one can easily forecast the experimental results by using this formula. This is called the *direct problem*. The *inverse problem*, the task to estimate the function $h_\alpha(\ln\alpha)$ given some data for the function $g(\tau)$, is much more difficult and cannot be done, as we will see, without introducing some prior knowledge.

In order to discuss this we will put the formula (4) into a more generic form. By discretizing the integral one introduces fixed points $\ln\alpha_j, j=1,...,M$ with constant spacing, the values $x_j = h_a(\ln\alpha_j)$ at these points are then the unknowns which are to be inferred from the data. Because furthermore the data are always superposed by some experimental errors we write generally

$$y_i = f_i(x_{1,...,M}) + \varepsilon_{i,} \quad i=1,...,N\,, \tag{6}$$

where we have written y_i for $g(\tau_i)$, f_i stands for the map between the two functions, ε_i denotes the experimental error at τ_i and $x_{1,...,M}$ is a shorthand notation for $\{x_1,...,x_M\}$. As discussed above we will assume that the errors are realizations of Gaussian random variables E_i with

$$\begin{aligned} &< E_i > \;=\; 0\,, \\ &Cov(E_i\, E_j) \;=\; C_{ij}, \quad C_{ii} = \sigma_i{}^2\,. \end{aligned} \tag{7}$$

Let us call eq. (6) the observation equation because it relates the observations $\{y_i\}$ to the unknowns $\{x_j\}$. The probability for the observations $\{y_i\}$ given the $\{x_i\}$ can be formulated as

$$\rho(y_{1,...,N} \mid x_{1,...,M}) \propto \exp\left(-\frac{1}{2}\sum_{k,l}(y_k - f_k(x_{1,...,M}))\; C^{-1}_{k,l}\;\; (y_l - f_l(x_{1,...,M}))\right), \tag{8}$$

i.e. the conditional probability is Gaussian with a mean given by the vector with components $f_i(x_{1..M})$ and with the covariance matrix given by $\mathbf{C}$. This is the information we infer from the assumptions on the errors.

From eqs. (6) and (7) it can be seen why it is not advisable to linearize the problem by taking the square root of the model (4) as it is sometimes suggested in the literature. The considerations above clearly show that this leads to a highly complicated error model.
Let us now discuss the inverse problem.

Bayes' Theorem and the Regularization Method

The Maximum a Posteriori (MAP) Estimator: From Bayes rule (see e.g. ref. 6) we obtain the probability of a realization $x_{1,\ldots,M}$ under the condition that a certain set of data $y_{1,\ldots,M}$ is given by:

$$\rho(x_{1,\ldots,M} \mid y_{1,\ldots,N}) = \frac{\rho(y_{1,\ldots,N} \mid x_{1,\ldots,M})\rho(x_{1,\ldots,M})}{\rho(y_{1,\ldots,N})}. \tag{9}$$

For a given set of data the distribution $\rho(y_{1,\ldots,N})$ is a constant with respect to $x_{1,\ldots,M}$, while $\rho(y_{1,\ldots,N} \mid x_{1,\ldots,M})$ depends on the parameters of the observation equation (see eq. (8)), and $\rho(x_{1,\ldots,M})$ is some so called *prior* distribution of $x_{1,\ldots,M}$. $\rho(x_{1,\ldots,M} \mid y_{1,\ldots,N})$ is also called the *a posteriori* distribution. This a posteriori distribution suggests a construction for an estimator $\hat{x}_{1,\ldots,M}$ for the realization of the process, under the condition that a set of data $y_{1,\ldots,N}$ and the observation equation are given.
The maximum a posteriori estimator (MAP estimator) is equal to that ‚distribution' $\hat{x}_{1,\ldots,M}$ for which the a posteriori distribution $\rho(x_{1,\ldots,M} \mid y_{1,\ldots,N})$ is maximum. Hence, it is defined by

$$\hat{x}_{1,\ldots,M} = \arg\max_{x_{1,\ldots,M}} \left\{ \rho(y_{1,\ldots,N} \mid x_{1,\ldots,M})\, \rho(x_{1,\ldots,M}) \right\}. \tag{10}$$

If we represent the conditional density $\rho(y_{1,\ldots,N} \mid x_{1,\ldots,M})$, by which the observation equation is defined, in the form

$$\rho(y_{1,\ldots,N} \mid x_{1,\ldots,M}) = e^{-U_B(y_{1,\ldots,N} \mid x_{1,\ldots,M})}, \tag{11}$$

and if we represent the prior probability $\rho(x_{1,\ldots,M})$ in the form

$$\rho(x_{1,\ldots,M}) = e^{-\lambda\, U_M(x_{1,\ldots,M})}, \tag{12}$$

then we can also write the MAP estimator as

$$\hat{x}_{1,\ldots,M} = \arg\min_{x_{1,\ldots,M}} \left\{ U_B(y_{1,\ldots,N} \mid x_{1,\ldots,M}) + \lambda U_M(x_{1,\ldots,M}) \right\}. \tag{13}$$

The factor λ in the prior density regulates the variance of the distribution of $x_{1,\ldots,M}$ around the most probable realization. If the data are not taken into account, then the most probable realization $x_{1,\ldots,M}$ is the one which minimizes $U_{\mathrm{M}}(x_{1,\ldots,M})$. By minimizing $U_{\mathrm{B}} + \lambda\, U_{\mathrm{M}}$, we also take into account the data, and the parameter λ controls the relative weight with which the prior knowledge enters into the estimation.

The MAP estimator for $x_{1,\ldots,M}$ now reads

$$\hat{x}_{1,\ldots,M} = \arg\min_{x_{1,\ldots,M}} \left\{ \sum_{k,l=1}^{N} \frac{1}{2} (y_k - f_k(x_{1,\ldots,M}))\, C_{k,l}^{-1}\, (y_l - f_l(x_{1,\ldots,M})) + \lambda U_{\mathrm{M}}(x_{1,\ldots,M}) \right\}. \tag{14}$$

For a complete definition of the estimator we still have to specify:

- the prior energy function $U_{\mathrm{M}}(x_{1,\ldots,M})$, i.e., the prior knowledge about the probabilities $\rho(x_{1,\ldots,M})$ for the distribution $x_{1,\ldots,M}$, irrespective of the data;
- the parameter λ, which regulates the strength of the variance in this probability distribution and therefore determines how much the prior knowledge enters into this estimation.

At first sight, the choice $\lambda = 0$ seems to be favorable, since in this case the prior energy function does not have to be specified at all. For the MAP estimator all $x_{1,\ldots,M}$ then have the same probability (i.e., $\rho(x_{1,\ldots,M})$ is a constant). This also means that no prior information whatsoever enters into the estimation. The MAP estimator has been reduced to the (nonlinear) least squares estimator.

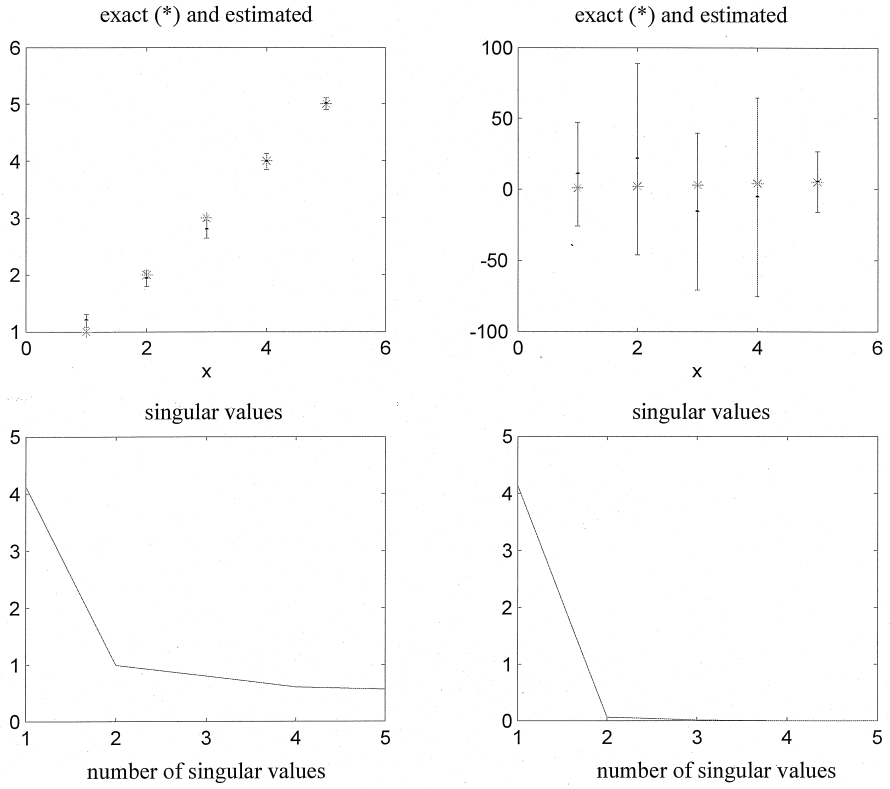

Fig. 2: True values, marked by an asterisk, and estimated values with confidence interval (error bars) for a problem with a well conditioned matrix (left) and with an ill-conditioned matrix (right). The ordered series of singular values is shown for each case in the bottom subfigure.

The effect and the necessity of the prior information can most easily be seen by considering a linear model, although the considerations are of course applicable to nonlinear models as well. If the map $f_i(x_{1,\dots,M})$ was linear we would have started with

$$y_i = g(\tau_i) = \int_{-\infty}^{\infty} d\ln\alpha\ K(\tau_i,\alpha)h(\ln\alpha) + \varepsilon_i, \quad i = 1,\dots,N, \tag{15}$$

so that by discretizing the integral we would have obtained

$$y_i = f_i(x_{1,\dots,M}) + \varepsilon_i = \sum_{j=1}^{M} K_{i,j}\, x_j + \varepsilon_i, \quad i = 1,\dots,N \tag{16}$$

with $K_{i,j} \propto K(\tau_i,\alpha_j)$. Now, the difficulty which one gets with the least squares estimator can easily be seen as the usefulness of the least squares estimator depends strongly on the

conditioning of the matrix $\mathbf{K} = \{K_{i,j}\}$. In Fig. 2 on the left-hand side an estimation for a well-posed problem is shown: the matrix $\mathbf{K}$ is well-conditioned as is seen in the lower subfigure, where the spectrum of the singular values is displayed. In the lower right subfigure the spectrum of a different matrix $\mathbf{K}$ is shown, already the third largest singular value is nearly zero. The consequence of such small singular values is that the confidence intervals of the estimates are getting very large as is seen in the upper right subfigure.

A matrix $\mathbf{K}$ with elements $K_{i,j}$ derived from the discretization of an integral is certainly ill-conditioned, and the conditioning will become worse the larger the number of points α_j, $j = 1,...,M$, for which $h_\alpha(\ln\alpha_j)$ shall be determined within the approximation of this discretization. Indeed, the larger the value of M, the closer neighboring α_j's (i.e., α_j and α_{j+1}) move together, and the more similar are the columns $\{K_{i,j},\ i = 1,...,N\}$ and $\{K_{i,j+1},\ i = 1,...,N\}$ of the matrix. But this implies that the matrix $\mathbf{K}$ becomes ‚more singular' and therefore the singular values are smaller.

Hence, the least squares estimator is in general inappropriate for such an inverse problem. The inverse problem, which corresponds to the solution of an integral equation, is therefore also called an ‚ill-posed' problem. (For a mathematical definition and treatment of ill-posed problems see also [7,8,9].) Without prior knowledge it is not possible to estimate the function $h_\alpha(\ln\alpha)$ with a reasonable estimation error on the basis of a finite set of data.

Regarding the choice of the regularization parameter there are different possible criteria. We will mention only two:

The discrepancy method:

This method is based on the assumption that the realization of the observational noise ε_i in the observed value y_i is of the order σ_i, and therefore the discrepancy for each observed value y_i, given by

$$\frac{1}{\sigma_i^2}\left(y_i - \sum_{j=1}^{M} K_{i,j}\, x_j\right)^2, \tag{17}$$

should be of order 1.

Therefore, λ is chosen such that

$$D(\hat{x}_{1,\ldots,M}|_{\lambda} \mid y_{1,\ldots,N}) \equiv \sum_{i=1}^{N} \frac{1}{\sigma_i^{\,2}} \left(y_i - \sum_{j=1}^{M} K_{i,j}\, \hat{x}_j|_{\lambda} \right)^2 = N\,. \tag{18}$$

The self-consistent method:

Let us suppose for the moment that the true solution $x_{1,\ldots,M}$ is known, as for instance in the simulation of data $y_{1,\ldots,N}$ for known $x_{1,\ldots,M}$ according to the observation equation. Obviously, we now may evaluate the mean square discrepancy

$$D(\lambda) \equiv \left\langle \left(x_{1,\ldots,M} - \hat{X}_{1,\ldots,M}|_{\lambda, Y_{1,\ldots,N}} \right)^2 \right\rangle \tag{19}$$

of the estimator $\hat{X}_{1,\ldots,M}|_{\lambda, Y_{1,\ldots,N}}$, where $X_{1,\ldots,M}$ and $Y_{1,\ldots,M}$ have been denoted by large letters to indicate that they have to be regarded as random variables.

Now we might choose λ such that $D(\lambda)$ is minimum. Hence, the optimal value λ^* would be determined by

$$\frac{\partial}{\partial\lambda} D(\lambda)\Big|_{\lambda=\lambda^*} \equiv \frac{\partial}{\partial\lambda} \left\langle \left(x_{1,\ldots,M} - \hat{X}_{1,\ldots,M}|_{\lambda, Y_{1,\ldots,N}} \right)^2 \right\rangle \Big|_{\lambda=\lambda^*} = 0.$$

In practice, however, the true solution $x_{1,\ldots,M}$ is never known. Nevertheless, instead of the true solution we may insert the optimal estimation $\hat{x}_{1,\ldots,M}|_{\lambda^*, Y_{1,\ldots,N}}$, i.e. the one determined with the parameter λ^*, and thereby obtain a criterion for λ^*:

$$\frac{\partial}{\partial\lambda} \tilde{D}(\lambda^*, \lambda) \equiv \frac{\partial}{\partial\lambda} \left\langle \left(\hat{x}_{1,\ldots,M}|_{\lambda^*, y_{1,\ldots,N}} - \hat{X}_{1,\ldots,M}|_{\lambda, Y_{1,\ldots,N}} \right)^2 \right\rangle \Big|_{\lambda=\lambda^*} = 0.$$

This expectation value first has to be computed explicitly as a function of λ and λ^*. This is possible for those cases where $X_{1,\ldots,M}|_{\lambda, Y_{1,\ldots,N}}$ depends linearly on the random variables $Y_{1,\ldots,N} = \{Y_1, Y_2, \ldots, Y_N\}$. Even in the general case, however, we may in principle estimate the expectation value for all pairs (λ, λ^*) [10,11]. In ref. 11 it was shown that the self-consistent method performs better than e.g. the discrepancy method.

We still have to discuss the choice of the prior energy function $U_{\mathrm{M}}(x_{1,\ldots,M})$. In most cases, one would like the distribution $x_{1,\ldots,M}$ to satisfy certain conditions, and $U_{\mathrm{M}}(x_{1,\ldots,M})$ is then constructed in such a way that those distributions $x_{1,\ldots,M}$ for which these conditions hold have the smallest energy (i.e., the largest probability).

Two frequently used energy functions are the following:

(1) If the norm of $x_{1,\ldots,M}$ shall be bounded the choice

$$U_{\mathrm{M}}(x_{1,\ldots,M}) = \sum_{i=1}^{M} x_i^{\,2} \tag{20}$$

is preferable. In these cases it is assumed that all x_i are mutually independent and normally distributed. The most probable configuration is $x_i = 0$ for all i.

(2) For the choice

$$U_{\mathrm{M}}(x_{1,\ldots,M}) = \sum_{i=2}^{M-1} \left(\frac{x_{i+1} - 2x_i + x_{i-1}}{\delta} \right)^2, \tag{21}$$

with some suitable constant δ, respectively, one expects the solution to have small second derivatives, i.e., the solution should be as smooth as possible.

In refs. 12 and 13 other energy functions that are suitable for other a priori knowledge about the solution are discussed. In this work we will use the energy function given in eq. (21) as we assume the solution to be smooth.

The Role of the Error Model: The Correlation of the Errors in Light Scattering

Coming back to the concrete problem, the analysis of light scattering data, according to eq. (14) we have to minimize the functional

$$V(\lambda) = \sum_{k,l=1}^{N} \left\{ \left[\hat{g}(\tau_k) - \hat{\beta} \left(\int_{-\infty}^{\infty} d\ln\alpha \; e^{-\tau_k/\alpha} \, h_\alpha(\ln\alpha) \right)^2 \right] C_{k,l}^{-1} \right.$$

$$\left. \left[\hat{g}(\tau_l) - \hat{\beta} \left(\int_{-\infty}^{\infty} d\ln\alpha \; e^{-\tau_l/\alpha} \, h_\alpha(\ln\alpha) \right)^2 \right] \right\} + \lambda \int_{-\infty}^{\infty} d\ln\alpha \; (h_\alpha''(\ln\alpha))^2 \tag{22}$$

with

$$C_{k,l} = \mathrm{Cov}[\hat{g}(\tau_k), \hat{g}(\tau_l)]. \tag{23}$$

The term in the last line of eq. (22) corresponds to the a priori knowledge that the solution should be smooth, i.e. it is the continous version of the energy function given by eq. (21). We

require that $h_\alpha(\ln\alpha) \geq 0$ for given λ so that we have to minimize $V(\lambda)$ subject to this constraint.

This minimization has to be done for given λ. The value of λ has to be determined by an appropriate criterion, e.g. the self-consistent method [11]. Furthermore, the covariance matrix $\mathbf{C}$ of the statistical errors of the estimates $\hat{g}(\tau_k)$ has to be determined. We will discuss two methods:

Estimating the statistical errors with a model

The estimation of the statistical errors with a model requires an estimate $\hat{g}(\tau_k)$ for the autocorrelation time function $g(\tau_k)$ at τ_k (with τ_k limited to values that can be written $t_i - t_j$ for some i, j). This can be obtained from the time series $\{n_{I_s}(t_1),...,n_{I_s}(t_{N'})\}$ of the scattered light according to

$$\hat{g}(\tau_k) = \frac{1/(N'-1)\sum_{i=1}^{N'-k}(n_{I_s}(t_i) - <\hat{n}>)(n_{I_s}(t_i+\tau_k) - <\hat{n}>)}{<\hat{n}>^2} \tag{24}$$

with

$$<\hat{n}> = 1/N' \sum_{j=1}^{N'} n_{I_s}(t_j). \tag{25}$$

However, two different estimators are implemented in currently available correlators. The first one is the so-called symmetric normalized estimator [14,4] and second one the compensated normalized estimator [4]. These two estimators have the advantage that they can be determined directly on the hardware during data acquisition. This advantage is exploited in the available hardware correlators, which yield estimates $\hat{g}(\tau_k)$ for the autocorrelation time function $g(\tau_k)$ as the result of a measurement.

The statistical errors of the estimates $\hat{g}(\tau_k)$ can be determined with a model proposed by Schätzel [15]. This model is based on the assumption that the detected intensity is a superposition of squares of Gaussian distributed electric field amplitudes and that the distribution of the number of photons arriving at the detector for a given intensity is a Poisson distribution. The model leads to an expression for the covariance matrix $\mathrm{Cov}(\hat{g}(\tau_k), \hat{g}(\tau_l))$ in dependence on the autocorrelation time function $g_{\mathrm{EE}}(\tau)$ of the field amplitude of the scattered photons [15]:

$$
\begin{aligned}
\mathrm{Cov}\big(\hat{g}(\tau_k),\hat{g}(\tau_l)\big) = N'^{-1}\Bigg\{ & \sum_{i=-K}^{K} \hat{g}_{\mathrm{EE}}(\tau_i)\big(\hat{g}_{\mathrm{EE}}(\tau_{i+k-l})+\hat{g}_{\mathrm{EE}}(\tau_{i+k+l})\big) \\
& + 2\hat{\beta}\sqrt{\hat{g}_{\mathrm{EE}}(\tau_k)\hat{g}_{\mathrm{EE}}(\tau_l)}\sum_{i=-K}^{K}\sqrt{\hat{g}_{\mathrm{EE}}(\tau_i)}\Big(\sqrt{\hat{g}_{\mathrm{EE}}(\tau_{i+k-l})}+\sqrt{\hat{g}_{\mathrm{EE}}(\tau_{i+k+l})}\Big) \\
& + 2\hat{\beta}\sum_{i=-K}^{K}\sqrt{\hat{g}_{\mathrm{EE}}(\tau_i)\;\hat{g}_{\mathrm{EE}}(\tau_{i+k})\;\hat{g}_{\mathrm{EE}}(\tau_{i+l})\;\hat{g}_{\mathrm{EE}}(\tau_{i+k+l})} \\
& + 4\;\hat{g}_{\mathrm{EE}}(\tau_k)\;\hat{g}_{\mathrm{EE}}(\tau_l)\sum_{i=-K}^{K}\hat{g}_{\mathrm{EE}}(\tau_i) \\
& - 4\hat{\beta}^{1/2}\;\hat{g}_{\mathrm{EE}}(\tau_l)\sqrt{\hat{g}_{\mathrm{EE}}(\tau_k)}\sum_{i=-K}^{K}\sqrt{\hat{g}_{\mathrm{EE}}(\tau_i)\;\hat{g}_{\mathrm{EE}}(\tau_{i+k})} \\
& - 4\hat{\beta}^{1/2}\;\hat{g}_{\mathrm{EE}}(\tau_k)\sqrt{\hat{g}_{\mathrm{EE}}(\tau_l)}\sum_{i=-K}^{K}\sqrt{\hat{g}_{\mathrm{EE}}(\tau_i)\;\hat{g}_{\mathrm{EE}}(\tau_{i+l})} \\
& + 2{<}\hat{n}{>}^{-1}\Big[\hat{g}_{\mathrm{EE}}(\tau_{k-l})+\hat{g}_{\mathrm{EE}}(\tau_{k+l})-2\;\hat{g}_{\mathrm{EE}}(\tau_k)\;\hat{g}_{\mathrm{EE}}(\tau_l) \\
& + 2\hat{\beta}^{1/2}\Big(\sqrt{\hat{g}_{\mathrm{EE}}(\tau_k)\hat{g}_{\mathrm{EE}}(\tau_l)\hat{g}_{\mathrm{EE}}(\tau_{k-l})}+\sqrt{\hat{g}_{\mathrm{EE}}(\tau_k)\hat{g}_{\mathrm{EE}}(\tau_l)\hat{g}_{\mathrm{EE}}(\tau_{k+l})}\Big)\Big] \\
& + {<}\hat{n}{>}^{-2}\,\delta_{kl}\;\big(1+\hat{g}_{\mathrm{EE}}(\tau_k)\big)\Bigg\}. \qquad (26)
\end{aligned}
$$

The value K in this equation must be chosen so large that $\hat{g}_{\mathrm{EE}}(\tau_N)\approx 0$ for $\tau \geq \tau_k$. The coherence parameter β can be estimated by extrapolation according to

$$\hat{\beta} = \lim_{\tau\to 0}\hat{g}(\tau). \qquad (27)$$

An estimate for the average number of photons $<n>$ arriving at the detector during the sampling time t_s can be computed according to eq. (25).

The determination of suitable values for the autocorrelation time function $\hat{g}_{EE}(\tau)$ in eq. (26) is more difficult which complicates the application of the error model. The expression suffers from the fact that the estimates $\hat{g}_{\mathrm{EE}}(\tau_k)$ can be negative in which case the expression $\sqrt{\hat{g}_{\mathrm{EE}}(\tau_k)}$ is not defined. These values have to be set to 0. Moreover, eq. (26) is based on the assumption that the correlation times are equally spaced. This is, however, not the case for the correlation times at which estimates $\hat{g}_{\mathrm{EE}}(\tau_k)$ are available after an experiment, and suitable values must be determined by interpolation.

On the other hand g_{EE} is given in eq. (5). An estimate $\hat{g}_{\mathrm{EE}}$ can also be obtained through the following procedure: First, $h_\alpha(\ln\alpha)$ is preliminarily estimated from the data using only the

diagonal elements of the covariance matrix $\mathbf{C}$. Afterwards, $\mathbf{C}$ is determined from eq. (26). With this result a better estimate for $h_\alpha(\ln\alpha)$ is obtained. This procedure could be repeated iteratively, but it turns out, that there is convergence after the first step already.

Estimating the statistical errors from the time series

The statistical errors of the estimates $\hat{g}(\tau_k)$ can also be determined without a model directly from the time series $\{n_{t_s}(t_1),...,n_{t_s}(t_{N'})\}$ of the scattered light:

$$\begin{aligned}\mathrm{Cov}\big(\hat{g}(\tau_k),\hat{g}(\tau_l)\big) \;=\; & N'^{-2} < \hat{n} >^{-4} \cdot \\ & \Big[\sum_{i,j=1}^{N'} \Big(n_{t_s}(t_i)\, n_{t_s}(t_i+\tau_k)\, n_{t_s}(t_j)\, n_{t_s}(t_j+\tau_l) - \hat{s}(\tau_k)\hat{s}(\tau_l) \Big) \\ & - \frac{2\hat{s}(\tau_l)}{< \hat{n} >} \sum_{i,j=1}^{N'} \Big(n_{t_s}(t_i)\, n_{t_s}(t_i+\tau_k)\, n_{t_s}(t_j) - < \hat{n} > \hat{s}(\tau_k) \Big) \\ & - \frac{2\hat{s}(\tau_k)}{< \hat{n} >} \sum_{i,j=1}^{N'} \Big(n_{t_s}(t_i)\, n_{t_s}(t_i+\tau_l)\, n_{t_s}(t_j) - < \hat{n} > \hat{s}(\tau_l) \Big) \\ & + \frac{4\hat{s}(\tau_k)\hat{s}(\tau_l)}{< \hat{n} >^2} \sum_{i,j=1}^{N'} \Big(n_{t_s}(t_i) n_{t_s}(t_j) - < \hat{n} >^2 \Big) \Big] \end{aligned} \tag{28}$$

with

$$\hat{s}(\tau_k) = 1/N' \sum_{i=1}^{N'} n_{t_s}(t_i)\, n_{t_s}(t_i+\tau_k)\,. \tag{29}$$

Because the time series $\{n_{t_s}(t_1),...,n_{t_s}(t_{N'})\}$ is stationary, the summations can be reordered and the covariance matrix $\mathrm{Cov}(\hat{g}(\tau_k),\hat{g}(\tau_l))$ can be estimated according to [15)]

$$\begin{aligned}\mathrm{Cov}\big(\hat{g}(\tau_k),\hat{g}(\tau_l)\big) = N'^{-1} < \hat{n} >^{-4} \cdot \Bigg[\sum_{i=-K}^{K} \Bigg(& \\ & \frac{1}{j_{\max}} \sum_{j=1}^{j_{\max}} n_{t_s}(t_{j+N+1})\; n_{t_s}(t_{j+N+1}+\tau_k)\; n_{t_s}(t_{i+j+N+1})\; n_{t_s}(t_{i+j+N+1}+\tau_l) - \hat{s}(\tau_k)\hat{s}(\tau_l) \\ & - \frac{2\hat{s}(\tau_l)}{< \hat{n} >} \sum_{i=-K}^{K} \Bigg(\frac{1}{j_{\max}} \sum_{j=1}^{j_{\max}} n_{t_s}(t_{j+N+1})\, n_{t_s}(t_{j+N+1}+\tau_k)\, n_{t_s}(t_{i+j+N+1}) - < \hat{n} > \hat{s}(\tau_k) \Bigg) \\ & - \frac{2\hat{s}(\tau_k)}{< \hat{n} >} \sum_{i=-K}^{K} \Bigg(\frac{1}{j_{\max}} \sum_{j=1}^{j_{\max}} n_{t_s}(t_{j+N+1})\, n_{t_s}(t_{j+N+1}+\tau_l)\, n_{t_s}(t_{i+j+N+1}) - < \hat{n} > \hat{s}(\tau_l) \Bigg) \\ & + \frac{4\hat{s}(\tau_k)\hat{s}(\tau_l)}{< \hat{n} >^2} \sum_{i=-K}^{K} \Bigg(\frac{1}{j_{\max}} \sum_{j=1}^{j_{\max}} n_{t_s}(t_{j+N+1})\; n_{t_s}(t_{i+j+N+1}) - < \hat{n} >^2 \Bigg) \Bigg] \end{aligned} \tag{30}$$

The value $j_{\max}$ in this equation is of the order of N' and must be chosen such that the $n_{I_s}(\cdot)$ are within the measured range. The value K has the same meaning as in the previous section (see eq. (26)) and must be chosen accordingly. This equation has the advantage that it can be evaluated much faster than eq. (28), because the value K is typically 100 to 1000 times smaller than the value N' [15].

With the currently used experimental setup, the estimates $\hat{g}(\tau_k)$ are computed on-line within the correlator during the measurement, and there is no further information available after the measurement. Therefore, eq. (30) cannot be evaluated. With a modified experimental setup it is, however, possible to store the time series $\{n_{I_s}(t_1),...,n_{I_s}(t_{N'})\}$ of the scattered light which allows the computation of the covariance matrix $\mathbf{C}$ with elements $\mathrm{Cov}(\hat{g}(\tau_k),\hat{g}(\tau_l))$ after the measurement. A proposal for such a modified setup is described in [16].

These considerations allow us to distinguish between three different methods in order to estimate the correlation time distribution:

- *the method with Schätzel variance:* The variances σ_k^2 of the estimates $\hat{g}(\tau_k)$ were determined according to the model of Schätzel, but only the diagonal elements of the covariance matrix $\mathbf{C}$ with elements $\mathrm{Cov}(\hat{g}(\tau_k),\hat{g}(\tau_l))$ were taken into account. In order to get numerical values for the variances, an intermediate result for the correlation time distribution was computed assuming that the statistical errors are independent and have all the same variance. From the intermediate spectrum the autocorrelation time function $g_{\mathrm{EE}}(\tau)$ and the variances $\mathrm{Cov}(\hat{g}(\tau_k),\hat{g}(\tau_l))$ were calculated according to eqs. (4) and (26), respectively. The final result for the correlation time distribution was obtained using those variances.
- *the method with Schätzel covariance:* In this method the full covariance matrix given by eq. (26) is taken into account.
- *the new method:* In this method, in which the time series $n_{I_s}(t)$ of the scattered photons must be stored, the full covariance matrix estimated by eq. (30) is taken into account.

Application to simulated data

Three time series with different lengths were simulated with Monte Carlo simulations. For the simulation 100 molecules with diffusion constants D_i (1,…,100) between 10^{-12} m^2/s and

10^{-9} m^2/s equally spaced on a logarithmic scale are chosen. The length of the wavevector $\mathbf{q}$ is fixed to $1.37 \cdot 10^{-7}$ m^{-1}. This leads to correlation times varying from $5 \cdot 10^{-6}$ s to $5 \cdot 10^{-3}$ s. These molecules execute a one dimensional random walk whereby for their space vector $\mathbf{r}_i$ the equation $\dot{r}_i(t) = \frac{\sqrt{2}}{\sqrt{\alpha_i q}} \eta(t)$ [6] is assumed. Here, $\eta(t)$ is a standard Gaussian random number and $\dot{r}_i(t)$ is the first derivative of the space vector with respect to the time. The electric field amplitude $E(t)$ is calculated assuming coherent scattering as $E(t) = \sum_{i=1}^{100} \sqrt{h_i}\, e^{i \mathbf{q} \cdot \mathbf{r}_i(t)}$ where $h_i = h_D(\ln D_i)$ [17].

From $E(t)$ the time series of the scattered intensity $I(t) = |E(t)|^2$ is obtained. Furthermore, the Poisson process is taken into account to obtain the time series $n_{t_s}(t)$ of the scattered photons. In order to do this the conditional probability of a Poisson random number n with density

$$p(n \mid I(t)) = e^{-\gamma t_s I(t)} \frac{(\gamma t_s I(t))^n}{n!} \tag{31}$$

is considered. Here, γ is the quantum efficiency of the detector [18]. In the following simulations the sampling time is set to 5 µs and γ to $8 \cdot 10^5 \frac{C^2}{N^2 s}$ leading to an expectation value $<n>$ for the photon time series of 4.0 ($<n> = \gamma \cdot t_s$). This is a typical value in real dynamic light scattering experiments. $n_{t_s}(t)$ is then a realisation of a random number with a density function given in eq. (31).

The lengths of the simulated time series are $N' = 5 \cdot 10^5$, $1 \cdot 10^6$, and $5 \cdot 10^6$. From each time series the correlation time distribution $h_\alpha(\ln \alpha)$ is estimated with the conventional method, the improved method, and the new method (see eq. (22)).

Fig. 3 shows estimates of h_α for the time series with $N' = 5 \cdot 10^5$. The method with Schätzel's variance and the method with Schätzel's covariance were not able to reconstruct the bimodal function. In contrast to these results, the new method (Fig. 3c) in which the covariance matrix is estimated directly from the time series is able to resolve the bimodal character of the distribution.

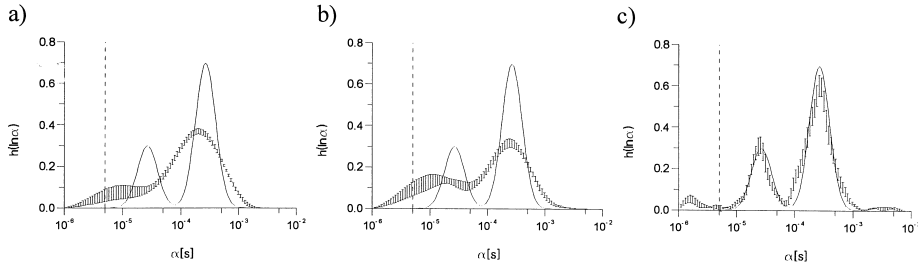

Fig. 3: The simulated correlation time distribution $h_\alpha(\ln\alpha)$ (solid line) and the estimated distribution (error bars) for the time series with $N'=5\cdot10^5$ for (a) the conventional method. In (b) and (c) the distributions estimated with new method from the same time series are seen. In (b) the covariance matrix is estimated with the model of Schätzel and in (c) it is directly estimated from the time series of the scattered photons. The dashed line marks the limit of the accessible range.

In Fig. 4 estimates that were done with a time series of length $N'=1\cdot10^6$ are shown. In this case only the method with Schätzel's variance is not able to reconstruct the bimodal character of the distribution.

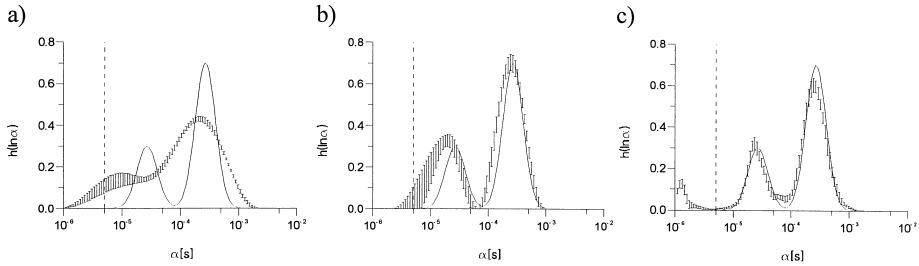

Fig. 4: The simulated correlation time distribution $h_\alpha(\ln\alpha)$ (solid line) and the estimated distribution (error bars) for the time series with $N'=1\cdot10^6$. The different estimators (a), (b), and (c) are defined in the caption of Fig. 3.

Fig. 5 shows that a time series of length $N'=5\cdot10^6$ is long enough that all methods are able to reconstruct the distribution well.

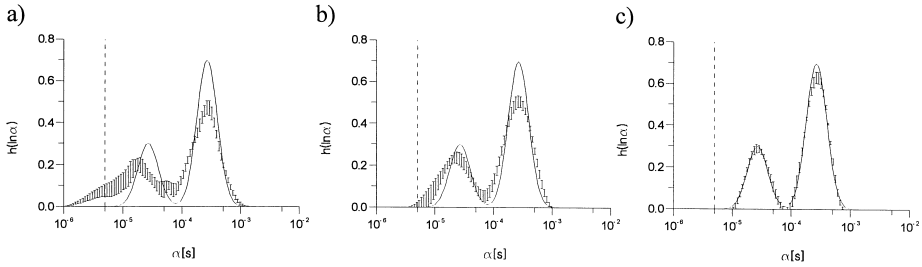

Fig. 5: The simulated correlation time distribution $h_\alpha(\ln\alpha)$ (solid line) and the estimated distribution (error bars) for the time series with $N' = 5 \cdot 10^6$. The different estimators (a), (b), and (c) are defined in the caption of Fig. 3.

In summary, for the distribution investigated in this section the measurement time must be 5000 times larger than the longest correlation time of the distribution to resolve the distribution neglecting the correlation of the statistical errors. Reducing the measurement time by a factor 5 the correlated errors must be considered but it was not necessary to store the time series of the scattered photons. If the measurement time is reduced by a factor 10 the time series must be stored to resolve the correlation time distribution. But it should be mentioned that these values depend on the distribution.

Concluding, it is clear that for very long time series the correlation in the statistical errors are not necessary to take into account in order to resolve a given correlation time distribution. But, reducing the measurement time the correlated errors become essential. Consequently, considering the correlated errors into the data analysis the resolution of the investigated distribution is improved and the measurement time can be reduced. This was shown for experimental data [16].

Analysis of Multi-Angle Data

In a multi-angle experiment the scattering of light on molecules with diffusion constants D is measured at angles θ_k, $k = 1,...,K$. Thus, the autocorrelation time function has also to be regarded as function of the angle θ and the experimental data are given by $g(\tau_i, \theta_k)$, $i = 1,...,N$, $k = 1,...,K$ and by the corresponding experimental errors.

In order to be able to find one estimate for all angles simultaneously it is necessary to rewrite the direct problem. One may first introduce the diffusion constants distribution $h_D(\ln D)$ which is independent from the measurement angle. Because of $\ln D = -\ln\alpha - 2\ln q(\theta)$ the

diffusion constants distribution $h_D(\ln D)$ can easily be related to the correlation time distribution $h_\alpha(\ln\alpha)$. In terms of $h_D(\ln D)$ the direct problem reads

$$g(\tau,\theta) = \beta(\theta)\left(\int_{-\infty}^{\infty} d\ln D\; K(\tau,\theta;D)\; h_D(\ln D)\right)^2 + \varepsilon(\tau,\theta) \tag{32}$$

with

$$K(\tau,\theta;D) = f_{\text{Mie}}(\ln D, q(\theta))\, e^{-\tau D q^2(\theta)} \tag{33}$$

where $f_{\text{Mie}}(\ln D, q(\theta))$ is given by Mie's Theory: It is proportional to the intensity of the light scattered by a sphere of radius a (i.e. a certain diffusion constant D) into the direction characterized by θ. Thus, one has $h_\alpha(\ln\alpha) = f_{\text{Mie}}(\ln D(\alpha), q(\theta))\cdot h_D(\ln D(\alpha))$. The relation between a and D is given by the Einstein-Stokes relation as

$$a = \frac{k_B T}{6\pi\eta D} \tag{34}$$

where T denotes the absolute temperature, η the viscosity of the solvent, and k_B the Boltzmann constant.

Mie's Theory provides a solution for the diffraction of a plane monochromatic wave by a sphere of radius a on the basis of electromagnetic theory. Various authors have dealt already with this problem [19,20,21]. In the present case, the solution from Born was used [22].

It is necessary to calculate the amplitude of the light scattered by a sphere in order to be able to evaluate eq. (32). This is typically done in spherical coordinates. Since for light scattering measurements on highly diluted solutions $k\tilde{r} >> 1$ holds (where $\tilde{r}$ is the distance from the scatterer to the detector and k is the absolute value of the wave vector in the medium surrounding the sphere), the radial components can be neglected. Furthermore, the common experimental setup is chosen such that $\varphi = 90° = const$ yielding $|E_\theta(\tilde{r},\theta,\varphi;a)| = 0$. Hence, the scattering intensity of a single sphere with radius a measured in a light scattering experiment and correspondingly $f_{\text{Mie}}(\theta,a)$ are given by

$$f_{\text{Mie}}(\theta,a) \propto \left|E_\varphi(\tilde{r},\theta,\varphi;a)\right|^2, \tag{35}$$

where E_φ is the component of the scattered electric field in direction φ.

Together with eq. (32) this allows to estimate $h_D(\ln D)$ from all angles simultanously. It should be noted that this has been reported before in the literature [23,24]. However, in these works the linearized direct model has been used which leads to severe problems regarding the

error model. In this work we will give results for multi-angle analysis with the nonlinear model as described above.

We now compare two different strategies: Either one collects all data $\hat{g}(\tau_i, \theta_k)$, $i = 1,.., N$, $k = 1,..., K$ into a large vector y_κ, $\kappa = 1,..., N \cdot K$. If one then discretizes the integral over $\ln D$ and introduces fixed points $\ln D_j$, $j = 1,..., M$ at constant spacing, one may write the direct problem as

$$y_\kappa = \beta_\kappa \left(\sum_{j=1}^{M} K_{\kappa,j} (h_D)_j \right)^2, \quad \kappa = 1,..., N \cdot K. \tag{36}$$

where β_κ is given by $\beta(\theta)$ with that value of θ which belongs to the index κ and $(h_D)_j$ is a shorthand notation for $h_D(\ln D_j)$. Thus we have the same type of problem as before and can estimate the diffusion distribution in the same way.

The other, more simple minded strategy would be to estimate the diffusion distribution $h_D(\ln D)$ for each angle. Then one could argue that the mean or some weighted mean of these estimates would be a decent estimate of the diffusion distribution based on the multi-angle data.

We will use both methods in the following and show that the results are different. This is not only an artifact or a matter of the experimental errors but a principle difference: Because the estimates are found by some Bayesian methods the mean or some weighted mean of the estimates for individual angles is not identical to the MAP estimator of the multi-angle data. In order to understand this we will study the case where only two angles θ_1, θ_2 are present. We will then write $y_{1,...,2N} = \left(\hat{g}(\tau_{i=1,...,N}, 1), \hat{g}(\tau_{i=1,...,N}, 2) \right)$. The distribution $\rho(D_{1,...,M} \mid y_{1,...,2N}, \theta_1, \theta_2)$, the maximum of which defines the multi-angle MAP estimator for $D_{1,...,M}$, can be written also as

$$\begin{aligned} \rho(D_{1,...,M} \mid y_{1,...,2N}, \theta_1, \theta_2) &= \frac{\rho(y_{1,...,2N} \mid D_{1,...,M}, \theta_1, \theta_2) \rho_{12}(D_{1,...,M})}{\rho(y_{1,...,2N})} \\ &= \frac{\rho(y_{1,...,N} \mid D_{1,...,M}, \theta_1) \rho(y_{N+1,...,2N} \mid D_{1,...,M}, \theta_2) \rho_{12}(D_{1,...,M})}{\rho(y_{1,...,2N})}, \end{aligned} \tag{37}$$

where we have used the fact that, given $D_{1,...,M}$, θ_1, θ_2, the data $y_{1,...,N}$ and $y_{N+1,...,2N}$ are independent and furthermore $y_{1,...,N}$ is independent of θ_2 and $y_{N+1,...,2N}$ is independent of θ_1. Now, also by definition it is

$$\rho(D_{1,\ldots,M} \mid y_{1,\ldots,N}, \theta_1) = \frac{\rho(y_{1,\ldots,N} \mid D_{1,\ldots,M}, \theta_1)\rho_1(D_{1,\ldots,M})}{\rho(y_{1,\ldots,N})} \tag{38}$$

and

$$\rho(D_{1,\ldots,M} \mid y_{N+1,\ldots,2N}, \theta_2) = \frac{\rho(y_{N+1,\ldots,2N} \mid D_{1,\ldots,M}, \theta_2)\rho_2(D_{1,\ldots,M})}{\rho(y_{N+1,\ldots,2N})}, \tag{39}$$

therefore also

$$\rho(D_{1,\ldots,M} \mid y_{1,\ldots,2N}, \theta_1, \theta_2) = \rho(D_{1,\ldots,M} \mid y_{1,\ldots,N}, \theta_1)\rho(D_{1,\ldots,M} \mid y_{N+1,\ldots,2N}, \theta_2) \cdot A \cdot B \cdot \tag{40}$$

with

$$A = \frac{\rho_{12}(D_{1,\ldots,M})}{\rho_1(D_{1,\ldots,M})\rho_2(D_{1,\ldots,M})} \tag{41}$$

and

$$B = \frac{\rho(y_{1,\ldots,N})\rho(y_{N+1,\ldots,2N})}{\rho(y_{1,\ldots,2N})}. \tag{42}$$

For estimates where the prior distributions $\rho(D_{1,\ldots,M})$ are constants the factor A is equal to one. Then, indeed, from eq. (40) one can derive that the maximum of $\rho(D_{1,\ldots,M} \mid y_{1,\ldots,2N}, \theta_1, \theta_2)$ is a weighted mean of the maxima of $\rho(D_{1,\ldots,M} \mid y_{1,\ldots,N}, \theta_1)$ and $\rho(D_{1,\ldots,M} \mid y_{N+1,\ldots,2N}, \theta_2)$. The factor B plays no role. Now, however, where we have to use a nonconstant prior distribution the factor A is not equal 1 and depends on the priors. Thus, the two estimators are different and must also lead to different results.

Application to simulated data: In order to compare these two different estimators we have applied them to data simulated with Monte Carlo simulations as described above. We will denote the different estimators as *multi-angle* estimator (the estimate gained from using the data all angles simultaneously), *single-angle* estimator (the estimate gained from using the data of one angle only), and *averaging* estimator (the estimate gained from averaging over the single-angle estimates weighted with their estimation errors).

Two time series were simulated for the angles $\theta = 50°, 60°$, and $90°$, respectively. The length of the time series was $N' = 10^8$ and for the wavelength of the laser $\lambda_L = 650$ nm was chosen. The other experimental parameters were $\eta = 1.0$ and $T = 300$ K.

The results for the simultaneous estimation are displayed in Fig. 6. The simulated distribution of radii $h_a(\ln a)$ (which is identical to $h_D(\ln D)$ up to a transformation of the abscissa, see

eq. (34)) is marked by the solid line. The distribution is bimodal with peaks at 550 nm and 900 nm. In Fig. 6a the solution of the multi-angle estimator is shown by the error bars. In Fig. 6b the solution obtained using the single-angle estimator is shown and in Fig. 6c the results obtained from averaging estimator are displayed. It can easily be seen that the estimate from the multi-angle estimator outperforms the averaging estimator: while the former reconstructs the bimodal character of the distribution, the latter cannot resolve this. This is, of course, a result of the fact that these details are not resolved by the single-angle estimator either.

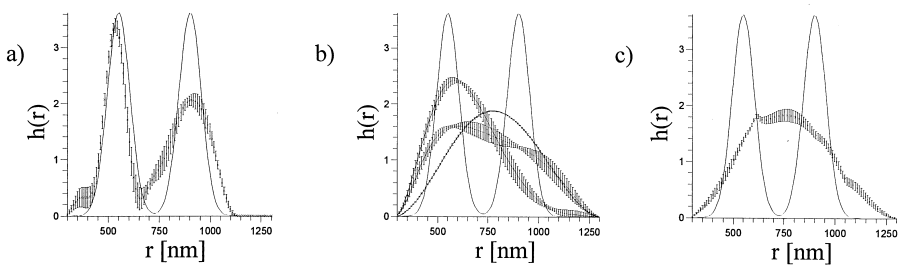

Fig. 6: The simulated radii distribution (solid line) and the estimated distribution (error bars) for the time series with $N' = 10^9$. (a) multi-angle estimator, (b) single-angle estimator, and (c) averaging estimator.

While these results again depend on the distribution to be estimated it shows that the effort for the implementation of an estimator for simultaneous estimation is justified by the superior results.

Summary and Conclusions

We have presented the regularization method for solving ill-posed inverse problems. The necessity to apply regularization methods for these problems was shown. Furthermore, some possibilities for the choice of the a priori knowledge and some criteria for choosing the regularization parameter were discussed. Moreover, the regularization method was embedded in Bayes' ansatz.

These general results for solving ill-posed inverse problems were applied to data from dynamic light scattering. In the first application the importance for considering the correlation of the errors of the autocorrelation time function was discussed. It was shown that the

estimation of the covariance of the errors computed directly from the time series of the scattered light leads to better results than the use of the model by Schätzel, but that already this use leads to an improvement compared to an analysis, in which the correlation of the experimental errors is neglected at all.

In a second example the evaluation of data measured at several angles was examined. It was shown through manipulation of Bayes' rule that the estimation with all angles simultaneously is in principle different from averaging over single estimates. This was confirmed by applying the estimators to data from Monte Carlo simulations. The multi-angle estimator performed much better than the averaging estimator.

We conclude that although data analysis in DLS is a topic that has been researched for a while there is still room for improvement, especially through the use of more detailed models. These enhanced models can greatly increase the benefit drawn from DLS as a method for characterizing macromolecules, e.g. by improving the resolution of the estimated distributions.

References

1. K. Schätzel,E. O. Schulz-Du Bois, *Infrared Phys.* **32,** 409 (1991)
2. K. Schätzel, *Appl. Phys.* **B 42**, 193 (1987)
3. K. Schätzel, *Inst. Phys. Conf.* **B 77**, 175 (1985)
4. K. Schätzel, R Peters, in: *Photon Corr. Spectr. Multicomponent System* (Ed. K. S. Schmitz) **1430,** 109 (1991)
5. B. J. Berne, R. Pecora, *Dynamic Light Scattering,* Wiley, New York 1976
6. J. Honerkamp, *Stochastic Dynamical Systems*, VCH, New York 1993
7. A. N. Tikhonov, V. Y. Arsenin, *Solutions of Ill-Posed Problems*, Wiley, New York 1977
8. C. W. Groetsch, *The Theory of Tikhonov Regularization for Fredholm Equations of the First Kind*, Pitman, London 1984
9. V. A. Morozov, *Methods for Solving Incorrectly Posed Problems*, Springer, Berlin 1984
10. J. Honerkamp, D. Maier, J. Weese, *J. Chem. Phys.* **98,** 865 (1993)
11. J. Weese, *Comp. Phys. Comm.* **77,** 429 (1993)
12. J. Honerkamp, *Statistical Physics,* Springer, Berlin 1998
13. T. Roths, D. Maier, Chr. Friedrich, M. Marth, J. Honerkamp, *Rheol. Acta* **39**, 163 (2000)
14. K. Schätzel, R. Drewel, S. Stimac, *J. Modern Optics* **35**, 711 (1988)
15. K. Schätzel, *Quantum Optics*, **2,** 287 (1990)
16. D. Maier, M. Marth, J. Weese, J. Honerkamp, *Appl. Opt.* **38**, 4671 (1999)
17. A. Einstein, *Ann. Phys.* **13,** 1275 (1910)
18. E. Jakeman, *J. Phys.: Gen. Phys.* **3,** 201 (1970)
19. M. Kerker, *The Scattering of Light and other Electromagnetic Radiation*, Academic Press, New York 1969
20. C. Bohren ,D. Huffman, *Absorption and Scattering of Light by Small Particles,* Wiley, New York 1983
21. J. Hansen, D. Maier, J. Honerkamp, W. Richtering, M. F. Horn, H. Senff, *J. Coll. Interf. Sci.* **215,** 72 (1999)
22. M. Born, E. Wolf, *Principles of Optics,* Pergamon Press, London 1959

23. C. Wu, K. Unterforsthuber, D. Lilge, E. Lüddecke, D. Horn, *Part. Part. Syst. Charact.* **11,** 145 (1994)
24. S. Provencher, P. Štepánek, *Part. Part. Syst. Charact.* **13,** 291 (1996)