Light scattering polydispersity analysis of molecular diffusion by Laplace transform inversion in weighted spaces

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Light scattering polydispersity analysis of molecular diffusion by Laplace transform inversion in weighted spaces

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Previous work on the use of singular systems for the inversion of photon correlation functions obtained in the analysis of molecular polydispersity by laser light scattering is extended to allow the imposition of a "profile" function, having the measured mean and polydispersity index, to localize the recovered solution and improve its resolution. This profile function is used to construct an appropriate orthonormal basis in a weighted L^2 space in which to expand the solution and also a basis of vectors for expanding the experimental data.

The spectrum of light scattered from a monochromatic laser beam by a suspension of monodisperse molecules undergoing Brownian diffusion is of Lorentzian shape with half-width Γ inversely proportional to the hydrodynamic radius of the molecules. Such a spectral measurement is normally performed by photon correlation techniques[1,2] in which the Fourier transform of this spectrum, namely an exponential correlation function $g(\tau)$ is derived. When more than one size of molecule is present a sum of exponential functions results:

$$g(\tau) = \int_0^\infty f(\Gamma) e^{-\Gamma\tau} d\Gamma. \tag{1}$$

The difficult problem of inverting this sum to recover the distribution $f(\Gamma)$ is well known and has enjoyed widespread discussion.[3-5] From a mathematical point of view we are faced with the ill-conditioned problem of the inversion of a finite, sampled, noise-contaminated Laplace transform; this problem, which also arises in a number of other disciplines, has no unique solution and extra *a priori* information must be adjoined in order to remove the ill conditioning (i.e., to regularize the problem). More information than the mean

$$\bar{\Gamma} = \int_0^\infty \Gamma f(\Gamma) d\Gamma \tag{2}$$

and the polydispersity index $Q = \text{Var } \Gamma/\bar{\Gamma}^2$, where

$$\text{Var } \Gamma = \int_0^\infty (\Gamma - \bar{\Gamma})^2 f(\Gamma) d\Gamma \tag{3}$$

which may both be obtained simply from the data $g(\tau)$[3,6,7] is to be sought.

In previous work[8-10] we have established the value of using *a priori* knowledge of the spread of molecular sizes present by restricting the support of the solution $\Gamma \in [a, b]$ and we have developed the formalism of singular function analysis, appropriate to deal with this problem.

This method was successfully used in analyzing simulated data with various values of the polydispersity index. However, the sharp truncation of the singular functions at the boundaries a and b had undesirable effects on the recovered solution, namely too much sensitivity to the position of $\bar{\Gamma}$ within the interval $[a, b]$ and some unphysical edge effects.

In this letter we present another way of restricting the possible spread of sizes in a more natural fashion, avoiding a sudden cutoff in the solution, and making *a priori* use of the measured mean $\bar{\Gamma}$ and polydispersity index Q of the distribution.

The method involves returning to an unrestricted solution on $[0, \infty]$, but using a "profile" function $f_0(\Gamma)$ which is large in the expected region of the solution and which tapers off smoothly to zero on either side.[11] This profile function is not meant to be a close approximation of the solution, but, as we shall see, is used to localize the solution and to provide a satisfactory set of orthonormal functions in which the solution may be expanded. The problem we wish to solve by the singular function method is the recovery of the function $\varphi(\Gamma)$, which, multiplied by the profile function $f_0(\Gamma)$ yields the distribution $f(\Gamma)$ we are seeking. We defer detailed mathematics to a fuller publication elsewhere[12] but give here the principle of the calculation and some preliminary results.

Formally, the problem may be written as

$$g(\tau_n) = \int_0^\infty e^{-\Gamma\tau_n} f_0(\Gamma) \varphi(\Gamma) d\Gamma. \tag{4}$$

This equation defines the operator K transforming the function $\varphi(\Gamma)$ into N sampled data values, $g(\tau_n) = (K\varphi)(\tau_n)$: $n = 1, \ldots, N$.

Its singular system consists of the set of singular functions $u_k(\Gamma)$, singular vectors $v_k(\tau_n)$ and singular values α_k related by the usual expressions[8]:

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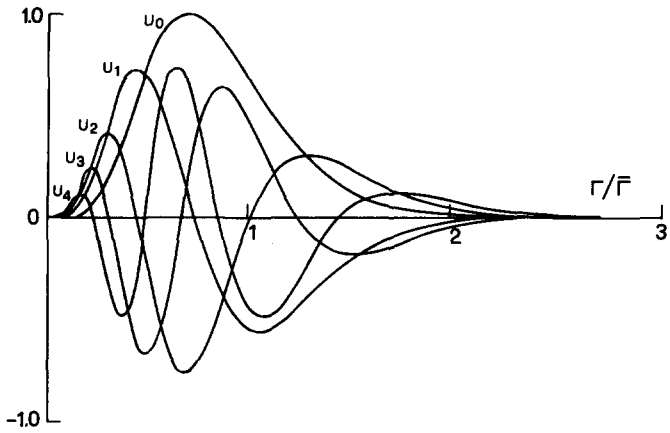

FIG. 1. Set of singular functions computed in the case of 32 linearly distributed points, spaced by the distance 0.45, for $\beta = 4$.

$$Ku_k = \alpha_k \mathbf{v}_k, \quad \text{and} \quad K^* \mathbf{v}_k = \alpha_k u_k, \tag{5}$$

where K^* denotes the adjoint operator of K, with respect to an inner product defined with weight w_n appropriate to the spacing of the data samples. In the case of equidistant points we have taken constant weights equal to the sampling distance, and in the case of exponential sampling, $\tau_n = \tau_1 \Delta^{n-1}$, we have taken $w_n = \tau_n \ln \Delta$.[9] To compute this singular system, one must find the eigenvalues α_k^2 and eigenvectors $\mathbf{v}_k$ of the operator KK^* since from Eq. (5), $KK^* \mathbf{v}_k = \alpha_k^2 \mathbf{v}_k$. These can be obtained by computing the eigenvalues α_k^2 and eigenvectors $\bar{\mathbf{v}}_k$ of the symmetric matrix

$$T_{nm} = \sqrt{w_n w_m} \int_0^\infty e^{-(\tau_n + \tau_m)\Gamma} f_0^2(\Gamma) d\Gamma, \tag{6}$$

where $\bar{\mathbf{v}}_k$ is related to $\mathbf{v}_k$ by

$$v_k(\tau_n) = \sqrt{w_n} \bar{v}_k(\tau_n). \tag{7}$$

The corresponding singular function is computed by[10,12]

$$u_k(\Gamma) = \frac{f_0(\Gamma)}{\alpha_k} \sum_{n=1}^{N} \sqrt{w_n} \bar{v}_k(\tau_n) e^{-\tau_n \Gamma}. \tag{8}$$

For a given choice of $f_0(\Gamma)$, these results may be stored once and for all, and the data analysis program merely yields the coefficients g_k of the expansion of the data $g(\tau_n)$ on the basis of the vectors $\bar{v}_k(\tau_n)$:

$$g_k = \sum_{n=1}^{N} \sqrt{w_n} g(\tau_n) \bar{v}_k(\tau_n). \tag{9}$$

The coefficients c_k of the solution $\varphi(\Gamma)$ expanded in the basis of singular functions $u_k(\Gamma)$

$$\varphi(\Gamma) = \sum_{k=0}^{N-1} c_k u_k(\Gamma) \tag{10}$$

are simply related to the computed g_k by $c_k = g_k/\alpha_k$ and the problem of recovering $\varphi(\Gamma)$ and thus $f(\Gamma) = f_0(\Gamma)\varphi(\Gamma)$ is formally solved:

$$f(\Gamma) = \sum_{k=0}^{N-1} \frac{g_k}{\alpha_k} f_0(\Gamma) u_k(\Gamma). \tag{11}$$

In practice, the above summation can only extend over a more limited number of terms K_s which depends on the rms error σ in the data and the singular value spectrum [typically for a σ of order 10^{-3}, $K_S \lesssim 6$)]. Theoretical values of σ as a function of experiment duration in the high counting rate limit are given in Ref. 5. The weighted singular functions $U_k(\Gamma) = f_0(\Gamma) u_k(\Gamma)$ are shown in Fig. 1 for a particular choice of profile, namely the gamma distribution (Schulz distribution):

$$f_0(\Gamma) = \frac{\beta^\beta}{(\beta - 1)!} \left(\frac{\Gamma}{\bar{\Gamma}}\right)^{\beta - 1} e^{-\beta(\Gamma/\bar{\Gamma})} \tag{12}$$

whose mean value $\bar{\Gamma}$ has been chosen equal to 1. The functions plotted relate to 32 linearly distributed points and are very similar to the set obtained using five exponentially spaced points.[12]

The method has been thoroughly tested with a great number of simulated and experimental data in order to optimize the choice of the parameter β, predict the resolution obtainable, and avoid artifacts. Our conclusions are summarized below.

The parameter β determines the polydispersity index $Q_{\max} = 1/\beta$ of the profile function which represents the upper limit of the relative variance recoverable with that particular choice of β.

Now there also exists a lower limit $Q_{\min}$ which is due to the enforced limitation of the summation in Eq. (11); the narrower the function $f(\Gamma)$, the more terms one needs for its reconstruction and the smaller $Q_{\min}$ needs to be.

Recoveries of functions having one or several peaks, each having a Q smaller than $Q_{\min}$, are likely to exhibit negative portions as illustrated on several examples with delta functions or narrow Schulz distributions (see Fig. 3).

TABLE I. The characteristics of the singular systems computed in the case of a linear distribution of points $\tau_n = (n-1)d$, $n = 1, 2, \ldots, 32$.

β	d	$Q_{\max} = 1/\beta$	Q_0 (emp.)	$Q_{\min}$	$R_{\min}$	$Q_{\exp}$
20	0.15	0.05	0.03 (0.035)	0.02	1.5	0.04
10	0.20	0.10	0.05 (0.07)	0.03	1.7	0.07
4	0.45	0.25	0.15 (0.15)	0.07	2.2	0.14
2	0.55	0.50	0.37 (0.25)	0.08	2.4	0.17
1.3	0.60	0.77	0.79 (0.40)	0.15	3.6	0.32

Note: Empirically, Q_0 must be replaced by the data in parentheses.

The Q_{min}, empirically determined by fitting with each β simulated data (with a noise level of 10^{-3}) corresponding to decreasing Q_{exp}, are shown in Table I, together with $Q_{max} = 1/\beta$.

We see that for a set of data corresponding to a given Q_{exp}, a whole range of β values seems available. One must, however, be aware of the fact that the building blocks for the recovered function $f_r(\Gamma)$ are the K_S profiled singular functions $U_0, \ldots, U_{K_S-1}$, the first one U_0 of polydispersity index Q_0, being the only one exhibiting a single extremum. Any linear combinations of the U_k which are to give a $Q \gtrsim Q_0$ are bound to exhibit several extrema, whereas for $Q < Q_0$ the overall shape of $f_r(\Gamma)$ is not *a priori* determined.

As a consequence, recovery from the set of data $\{g(\tau_n)\}$ of a function $f(\Gamma)$ for which only Q_{exp} and $\bar{\Gamma}_{exp}$ are known requires a choice of the largest β in the table such that $Q_{min} < Q_{exp} \lesssim Q_0$, the units of τ and Γ being chosen respectively equal to $(\bar{\Gamma}_{exp})^{-1}$ and $(\bar{\Gamma}_{exp})$.

Examples of such recoveries are given for simulated and experimental data in Figs. 2, 3 and 4. Single-peaked distributions, symmetric or not, are well reconstructed in the whole range $0.02 < Q_{exp} \lesssim 0.5$ always yielding a closer fit to the simulated function than the Gaussian method[6,7] which is known to become unreliable for $Q_{exp} \gtrsim 0.2$ and/or unsymmetric shapes.

Now, if some additional *a priori* knowledge rules out a single-peaked function, the resolution can be pushed further by increasing β, the above condition being replaced by $Q_{min} < Q_{exp} < Q_{max}$ (see Fig. 3, with $\beta = 4$).

The problem of extracting two narrow peaks can be formulated more precisely as follows. Let $R > 1$ be the ratio of their peak positions. Resolution of these two peaks is first limited by Q_{min}, which determines the relative width of each recovered peak. An evaluation of that limit R_{min} is shown in Table I, assuming the two peaks to be Gaussian, equal in height, and demanding $f(\Gamma)$ to drop by 30% between the peaks. The corresponding polydispersity $Q_{exp} = (R_{min} - 1)^2/(R_{min} + 1)^2$ is shown in the next column. As mentioned above, with no *a priori* knowledge of the shape of $f(\Gamma)$, a profile function should be chosen so that $Q_{min} < Q_{exp} < Q_0$. As seen in Table I, established for $\sigma = 10^{-3}$, this limits the resolution ratio R in this case to $R_{min} \gtrsim 1.7$. For higher resolution *a priori* knowledge that $f(\Gamma)$ is not single peaked allows a narrower profile function, such that $Q_0 < Q_{exp} < Q_{max}$, to be used. It should not be forgotten that reconstructions at different scattering angles may give further useful information to narrow the range of acceptable solutions.

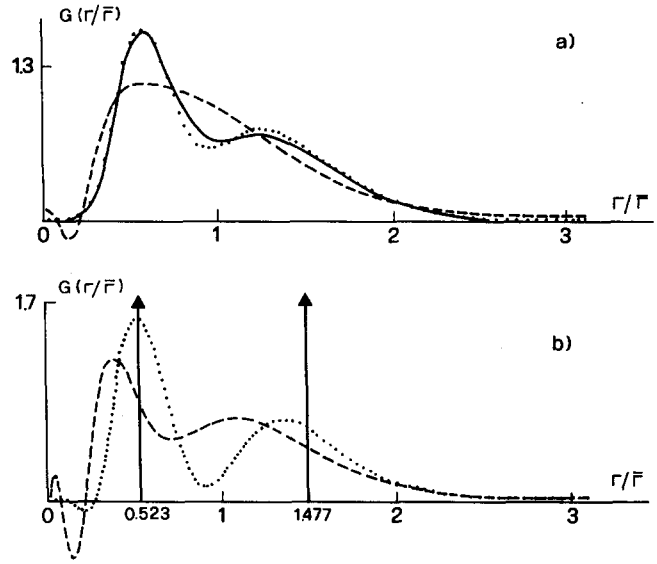

FIG. 3. Reconstruction of a double-peaked distribution with $Q_{exp} \simeq 0.23$. With no *a priori* knowledge of the shape of the function, one chooses a reconstruction with $\beta = 2$ (---). Additional knowledge that the function is not single peaked allows us to choose $\beta = 4$ (dotted line). Case (a): two narrow Schulz functions with $\bar{\Gamma}_1 = 0.63$, $\bar{\Gamma}_2 = 1.38$, and $\beta_1 = \beta_2 = 13$. Case (b): two delta functions with $\Gamma_1 = 0.52$ and $\Gamma_2 = 1.48$.

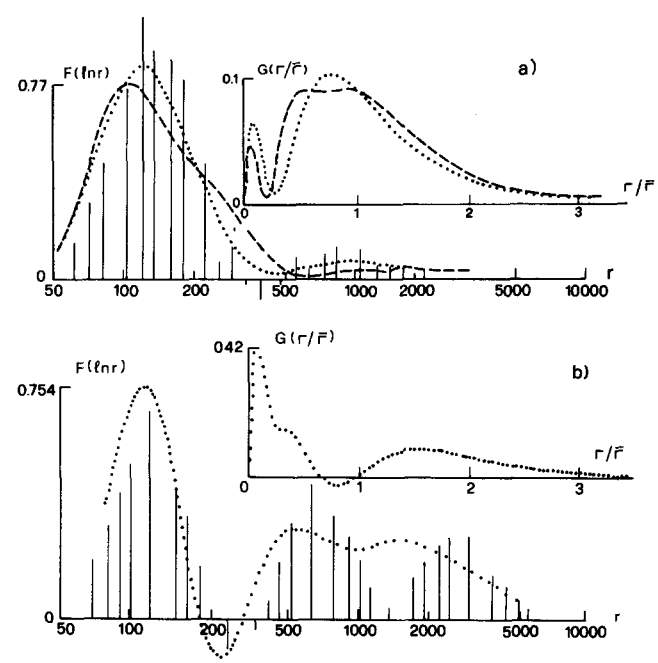

FIG. 4. Intensity distribution $F(\ln r)$ as a function of r, measured in angstroms extracted from experimental data on coagulating vesicle suspensions 30 min [case (a)] and 135 min [case (b)] after the reaction has started. The vertical lines were computed with the exponential sampling method with $\omega_0 = 4$, and five consecutive shifts. In the upper right-hand corner are plotted the corresponding reconstructed distributions $f(\Gamma)$ in the Γ space (dots correspond to $\beta = 1.3$ and dashes to $\beta = 2$).

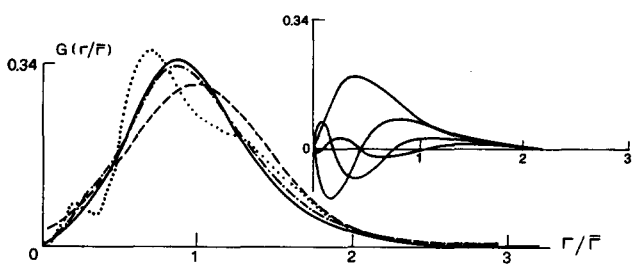

FIG. 2. Reconstruction of a single-peaked $f(\Gamma)$ simulated by a linear combination of two Schulz functions of equal amplitude and mean, but different polydispersities, shown by the solid line. As Q_{exp} was found equal to 0.2, a reconstruction with $\beta = 2$ was chosen (- · -); the four components used, c_iU_i, $i = 0, \cdots 3$, are shown in the right-hand corner. A Gaussian distribution having the same polydispersity is drawn with a dashed line. An attempt to increase β to 4 brings Q_{exp} into the interval $[Q_0, Q_{max}]$ and the reconstructed function exhibits more than one peak (dotted line).

Finally, in Fig. 4 we present some size polydispersity analysis on real data, the plotted function $F(\ln r)$ being such that

$$F(\ln r)|d \ln r| = f(\Gamma)|d\Gamma|, \tag{13}$$

where r is the radius of the particle. For the sake of comparison, results of the previously used exponential sampling method[13] are shown on the plot; the agreement between these two significantly different methods is remarkably good.

In conclusion we have shown that use of the measured mean and polydispersity index in the inversion procedure by their incorporation into a profile function can be accomplished using a set of basis functions in a suitable weighted space. This *a priori* knowledge is very effective in improving resolution of closely spaced peaks in the solution and the method, which is still linear, can therefore be used for rapid and convenient numerical computations.

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