ON THE DEFINITION AND USE OF DEVIATION FUNCTIONS FOR TREATMENT OF QUASI-ELASTIC LIGHT SCATTERING DATA

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

A theory for *deviation functions* defined as the deviation from strict gaussian behaviour of electric field correlation functions obtained from Quasi-Elastic Light Scattering experiments is presented. Its application to systems with different types of particle size distributions is treated both theoretically and by numerical examples. Expressions are given for distributions where the correlation function can be expressed as a Laplace transform in closed form. The theory is also compared with experiments on solutions of polymers with a variety of molecular mass distributions. It is concluded that even if the procedure based on deviation functions cannot compete with other numerical inversion methods in the direct determination of molecular size distributions it may substantially help to visualize the magnitude of the effect of polydispersity and serve as a prerequisite for a decision concerning how far it is meaningful to pursue more precise calculations. This is essentially equivalent to a judgement of the noise level of the experiment and of the "information content" to be expected.

In the type of fluctuation spectroscopy experiment normally termed Quasi-Elastic Light Scattering (QELS) correlation times characteristic of certain dynamic processes are determined. When the technique is applied to dilute polymer solutions the characteristic correlation times obtained are directly related to the diffusion coefficient of the polymer species in the medium. Since there is a unique relation between molecular size and diffusion coefficient such experiments provide information of particle size and particle size distributions.

General theory[1] shows that for a normal QELS experiment the basic intensity correlation data $G(\tau)$, where τ is the correlation time, follows the mathematical form

$$G(\tau) = A\{1 + \beta[g(\tau)]^2\} , \qquad (1)$$

where A and β are constants characteristic of the particular experiment and equipment. For an experiment with only one *characteristic correlation time*, Γ^{-1}, the *electric field correlation function* $g(\tau)$ reduces to

$$g(\tau) = \exp(-\Gamma\tau)\,. \tag{2}$$

For simplicity the parameter Γ will sometimes be referred to as "correlation frequency". If the dynamic process giving rise to the QELS effect is the translational diffusion of a single species one can show[1] that

$$\Gamma = q^2 D\,, \tag{3}$$

where D is the diffusion coefficient and q is the value of the scattering vector defined by

$$q = (4\pi n/\lambda)\sin^2(\theta/2) \tag{4}$$

and λ is the wavelength of light in vacuum. Obviously $G(\tau)$ will become equal to A for large values of τ. Hence the numerical value of A is sometimes called "baseline".

THEORETICAL

In case of more than one dynamic process (e.g. species of different size diffusing as for a polydisperse polymer) there will be a *distribution* of characteristic correlation times (or more precisely correlation frequencies), $\Psi(\Gamma)$, and then the correlation function will be given by

$$g(\tau) = \int_0^\infty \psi(\Gamma)\exp(-\Gamma\tau)\mathrm{d}\Gamma \tag{5}$$

with

$$\int_0^\infty \psi(\Gamma)\mathrm{d}\Gamma = 1 \tag{6}$$

since $\psi(\Gamma)$ is normalized. Obviously, from Eq. (5), $g(\tau)$ is the Laplace transform, Ψ, of $\psi(\Gamma)$, i.e. by normal notation

$$\Psi(\tau) = \int \psi(\Gamma)\exp(-\Gamma\tau)\mathrm{d}\Gamma \tag{7}$$

and

$$g(\tau) = \Psi(\tau)\,. \tag{8}$$

It is clear that a discussion of how $g(\tau)$ is numerically affected by different distributions $\psi(\Gamma)$ is greatly simplified by selecting such functions ψ that give a Laplace transform Ψ in closed form. Model calculations for such cases will be presented in a later section in this paper.

In the practical application of QELS to macromolecular systems there are some not fully solved questions[2] concerning the analysis of $g(\tau)$ in terms of the normalized distribution of correlation times, $\psi(\Gamma)$.

In the present paper we will discuss these problems in a different way trying to relate the *distribution function* ψ to the *deviation* of $g(\tau)$ from a single exponential form. Such "deviation" discussions have proved to be quite efficient in classical diffusion studies[3,4]. This is particularly the case when polydispersity or multicomponent effects are investigated. Often it is illustrative to relate the magnitude and form of the deviation for a given average value $\langle\Gamma\rangle$ to the sample molecular size distribution.

The concept of deviation functions have previously been utilized in many branches of physical chemistry (cf. excess functions in thermodynamics[5]) and in particular in the quantitative analysis of multicomponent diffusion situations[4,6]. Although the deviation function approach has the same information content as other data treatments, it often allows a more practical understanding of the experimental results. It certainly helps to scrutinize the basic data since the deviation plots are sensitive to minute changes in the numerical values. The analysis presented here, in a sense "linear in Γ", is particularly useful in cases when the information content in the data covers only a relatively restricted range (e.g. macromolecular polydispersity). Widely separated time modes (distributions) should be treated in a different manner.

For further reference we will introduce the following definitions concerning averages in terms of the first and second moment, $\langle\Gamma\rangle$ and $\langle\Gamma^2\rangle$, respectively, as well as the distribution width σ^2 and the relative distribution width ρ^2 for the distribution function in question as given by the following relations:

$$\langle\Gamma\rangle = \int_0^\infty \Gamma\psi(\Gamma)\mathrm{d}\Gamma \tag{6a}$$

$$\langle\Gamma^2\rangle = \int_0^\infty \Gamma^2\psi(\Gamma)\mathrm{d}\Gamma \tag{6b}$$

$$\sigma^2 = \langle\Gamma^2\rangle - \langle\Gamma\rangle^2 \tag{6c}$$

$$\rho^2 = \sigma^2/\langle\Gamma\rangle^2 = \langle\Gamma^2\rangle/\langle\Gamma\rangle^2 - 1 . \qquad (6d)$$

The Deviation Function and Its Basic Properties

From relation (5) we immediately have that

$$\lim_{\tau \to 0} g(\tau) = \int_0^\infty \psi(\Gamma)\mathrm{d}\Gamma = 1 \qquad (9)$$

$$\lim_{\tau \to \infty} g(\tau) = 0 . \qquad (10)$$

The derivative of g with respect to τ is given by

$$g'(\tau) = \int_0^\infty \psi(\Gamma)\Gamma\exp(-\Gamma\tau)\mathrm{d}\Gamma \qquad (11)$$

and

$$\lim g'(\tau) = -\int_0^\infty \Gamma\psi(\Gamma)\mathrm{d}\Gamma = -\langle\Gamma\rangle , \qquad (12)$$

where $\langle\Gamma\rangle$ is the average value of Γ (the first cumulant[2]). The numerical value, p, of the first cumulant can be determined from the experimental data and a reference function $g_0(\tau)$ can be defined according to

$$g_0(\tau) = \exp(-p\tau) . \qquad (13)$$

From this a *deviation function*, $\omega(\tau)$, is defined

$$\omega(\tau) = g(\tau) - g_0(\tau) . \qquad (14)$$

It is easily shown that $\omega(\tau)$ is a function for which $\omega(0) = 0$ and $\omega(\infty) = 0$. The integral of $\omega(\tau)$ over all correlation times gives an interesting property. This integral is experimentally accessible according to its definition

$$I_1 = \int_0^\infty \omega(\tau)\mathrm{d}\tau \tag{15}$$

and from the previous relations

$$I_1 = \int_0^\infty\int_0^\infty \psi(\Gamma)\exp(-\Gamma\tau)\mathrm{d}\Gamma\mathrm{d}\tau - \int_0^\infty \exp(-p\tau)\mathrm{d}\tau = \int_0^\infty (1/\Gamma)\psi(\Gamma)\mathrm{d}\Gamma - 1/p\,. \tag{16}$$

The first term in Eq. (*16*) defines the average of the characteristic correlation time Γ^{-1}, i.e.

$$\langle\Gamma^{-1}\rangle = \int_0^\infty (1/\Gamma)\psi(\Gamma)\mathrm{d}\Gamma \tag{17}$$

and we have

$$\langle\Gamma^{-1}\rangle = I_1 + p^{-1}\,. \tag{18}$$

Some further properties of the deviation function may be derived. Writing Eq. (*14*) in explicit form we have

$$\omega(\tau) = \int_0^\infty \psi(\Gamma)\exp(-\Gamma\tau)\mathrm{d}\Gamma - \exp(-p\tau) \tag{14a}$$

and hence the derivative

$$\omega'(\tau) = \int_0^\infty \psi(\Gamma)\Gamma e^{-\Gamma\tau}\mathrm{d}\Gamma - pe^{-p\tau}\,. \tag{19}$$

If the maximum (or minimum) of $\omega(\tau)$ occurs for $\tau = \tau_m$, where $\omega'(\tau_m) = 0$ one finds

$$\langle\Gamma e^{-\Gamma\tau_m}\rangle = \int_0^\infty \psi(\Gamma)\Gamma e^{-\Gamma\tau_m}\mathrm{d}\Gamma = pe^{-p\tau_m}\,. \tag{20}$$

The maximum value itself is given by

$$\omega_{\max} = \omega(\tau_m) = \int_0^\infty \psi(\Gamma)\Gamma e^{-\Gamma\tau_m}\mathrm{d}\Gamma - e^{-p\tau_m} =$$

$$= g(t_m) - e^{-p\tau_m} = e^{-p\tau_m}\,[g(t_m)\,e^{-p\tau_m} - 1]\,. \tag{21}$$

One also has the following average directly

$$\langle e^{-\Gamma\tau_m}\rangle = \int_0^\infty \psi(\Gamma)e^{-\Gamma\tau_m}d\Gamma = g(\tau_m)\,. \tag{22}$$

Let us finally discuss the second derivatives and the inflexion points, i.e.,

$$\omega''(\tau) = \int_0^\infty \psi(\Gamma)\Gamma^2 e^{-\Gamma\tau}d\Gamma - p^2e^{-p\tau} \tag{23}$$

which gives

$$\langle \Gamma^2 e^{-\Gamma\tau}\rangle = p^2e^{-p\tau} + \omega''(\tau) \tag{24}$$

and at an inflexion point $\tau = \tau_{\mathrm{inf}}$ where $\omega'' = 0$ one finds

$$\langle \Gamma^2 e^{-\Gamma\tau_{\mathrm{inf}}}\rangle = p^2e^{-p\tau_{\mathrm{inf}}}\,. \tag{25}$$

From these expressions one may define a measure of the width of the distribution, *m*, according to

$$m = \langle \Gamma^2 e^{-\Gamma\tau_{\mathrm{inf}}}\rangle\langle e^{-\Gamma\tau_m}\rangle/\langle \Gamma e^{-\Gamma\tau_m}\rangle^2\,. \tag{26}$$

From Eqs (*20*), (*22*), and (*25*) we get

$$m = g(\tau_m)e^{-p(\tau_{\mathrm{inf}} - 2\tau_m)}\,. \tag{27}$$

The main results are contained in relation (*17*) as well as the relations basic to and including Eq. (*27*).

EXPERIMENTAL

Standard polystyrene (PS) from Pressure Chem. Co., M_w 498 000 (M_w/M_n < 1.06, batch 5a) and M_w 1800 000 (M_w/M_n < 1.2, batch 14a), were used. The broad polystyrene sample (Polystyrol IIID, BASF) was characterized[7] previously (M_w 295 000, $M_w/M_n \approx 4.59$). Polyethylene oxide (PEO) standard sample (M_w 150 000, M_w/M_n < 1.05) was a product of Polymer Laboratories.

The QELS experimental setup used, preparation and filtration of solutions were described recently[8]. It consists of a coherent Super-Graphite CR-4 argon-ion laser (Coherent Laser Division, Palo Alto, CA, U.S.A.) equipped with an intra-cavity etalon and tuned to 514.5 nm, a Hamamatsu R 268 photomultiplier tube (Hamamatsu Photonics K K, Japan), an amplifier-discriminator supplied by

Lindmark Innovation AB, Sweden and a 64 channel Langley–Ford digital correlator (Langley–Ford Instruments, Amherst, MA, U.S.A.). The polystyrene experiments were performed in toluene and the polyethylene oxide experiments in water solutions.

Calculation of experimental deviation functions. We refer to data obtained from a normal QELS experiment with a multichannel correlator. Let n_i be the accumulated number of counts in channel i of the correlator and let A be the corresponding number for the "baseline" (calculated or measured), see Eq. (*1*). For channels equidistantly spaced in time (channel width $\Delta\tau$) the correlation time is given by

$$\tau_i = i\,\Delta\tau\,. \tag{28}$$

To obtain the "initial" number of counts n_0, i.e. the number of counts in a channel zero, n_i for the first few channels is plotted versus τ_i (or i) and extrapolated to correlation time zero. The experimental correlation function g_i is then calculated according to

$$g_i = [(n_i - A)/(n_0 - A)]^{1/2} = g(\tau_i)\,. \tag{29}$$

By comparison with Eq. (*1*) one finds $\beta = n_0/A - 1$. From Eq. (*29*) the derivative $g'(\tau_i)$ of the correlation function with respect to τ can be found by an appropriate numerical derivation procedure. Extrapolation to $\tau = 0$ gives $\langle\Gamma\rangle = p$. In the same manner the second derivative $g''(\tau_i)$ can be calculated and extrapolated to $\tau = 0$ giving an intercept equal to $\langle\Gamma^2\rangle$. From these values the relative distribution width, ρ^2, can be obtained according to Eq. (*6d*). $\langle\Gamma\rangle$ can also be obtained by taking the derivative of the function $-\ln g_i$ with respect to τ and extrapolating to $\tau = 0$. This is a more reliable extrapolation and has been used in this work. A second order polynomial fit has been found to often give the best results in the extrapolation. The experimental deviation function, $\omega(\tau_i)$, is finally calculated according to

$$\omega(\tau_i) = g(\tau_i) - \exp(-p\,\tau_i)\,. \tag{30}$$

The first and sometimes even the second channel contain errors due to fast correlations residing in the electronics, the PM tube, etc. Hence, in the extrapolations to obtain A and $\langle\Gamma\rangle$ as described above, it is good practice not to include these channels. This procedure was followed when processing the experimental data presented here.

Both for the data treatment and for the model calculations the Macintosh software program KaleidaGraph™ was used.

RESULTS AND DISCUSSION

Model Calculations for Discrete Distributions

In order to get a better feeling for the functional shape and numerical magnitude of the deviation functions for QELS some model calculations were performed for discrete distributions of the characteristic correlation time, see Case I and Case II below.

Let us assume that the polymer sample contains N infinitely sharp fractions each with a characteristic correlation frequency Γ_i, $i = 1, \ldots, N$, and represented by the weight fraction w_i. This situation is denoted Case I. For the distribution function we then have

$$\psi(\Gamma) = \sum w_i \delta(\Gamma - \Gamma_i) , \qquad i = 1, \ldots, N \tag{31}$$

$$\sum w_i = 1 , \tag{32}$$

where δ denotes the Kronecker delta function. The various averages are given by the following relations:

$$\langle \Gamma \rangle = \sum \Gamma_i w_i \tag{32a}$$

$$\langle \Gamma^2 \rangle = \sum \Gamma_i^2 w_i \tag{32b}$$

$$\sigma^2 = \langle \Gamma^2 \rangle - \langle \Gamma \rangle^2 \tag{32c}$$

$$\rho^2 = \sigma^2 / \langle \Gamma \rangle^2 = \langle \Gamma^2 \rangle / \langle \Gamma \rangle^2 - 1 . \tag{32d}$$

The correlation function becomes

$$\psi(\tau) = \int_0^\infty \Psi(\Gamma) \exp(-\Gamma\tau) \mathrm{d}\Gamma = \sum w_i \exp(-\Gamma_i \tau) = g(\tau) , \tag{33}$$

where the summation is performed over $i = 1, \ldots, N$. From Eq. (*33*) we have the following relations useful for the experimental definition of the deviation functions

$$g'(\tau) = -\sum w_i \Gamma_i \exp(-\Gamma_i \tau) \tag{34}$$

$$g'(0) = -\sum w_i \Gamma_i = -\langle \Gamma \rangle = -p . \tag{35}$$

We now obtain the deviation function $\omega(\tau)$ and its derivatives according to

$$\omega(\tau) = g(\tau) - g_0(\tau) = \sum w_i \exp(-\Gamma_i \tau) - e^{-p\tau} \tag{36}$$

$$\omega'(\tau) = -\sum w_i\Gamma_i\exp(-\Gamma_i\tau) + p\mathrm{e}^{-p\tau} \tag{37}$$

$$\omega''(\tau) = \sum w_i\Gamma_i^2\exp(-\Gamma_i\tau) - p^2\mathrm{e}^{-p\tau} . \tag{38}$$

Obviously the first cumulant, $\langle\Gamma\rangle = p$, can be directly obtained from experimental data (slope of $g(\tau)$ at the origin). If the precision of the data is sufficient, one may read the correlation time coordinate τ_m for the maximum directly from a plot of $\omega(\tau)$ and obtain τ_{inf} for the inflexion point by numerical differentiation of $\omega(\tau)$. This would correspond to the two relations $\omega'(\tau_m) = 0$ and $\omega''(\tau_{inf}) = 0$ and the distribution measure m could be calculated according to Eq. (*27*). On this scheme it is relatively easy to calculate the deviation behaviour assuming an appropriate set of paired distribution data $\{\Gamma_i, w_i\}$.

The previous expressions reduce to very simple formulas in the case of a mixture of only two sharp fractions (denoted Case II) for which we may write $\Gamma_1 = a$ and $\Gamma_2 = b$ giving

$$\omega(\tau) = g(\tau) - g_0(\tau) = (w_1\mathrm{e}^{-a\tau} + w_2\mathrm{e}^{-b\tau}) - \mathrm{e}^{-p\tau} \tag{39}$$

$$\omega'(\tau) = -(w_1a\mathrm{e}^{-a\tau} + w_2b\mathrm{e}^{-b\tau}) + p\mathrm{e}^{-p\tau} \tag{40}$$

$$\omega''(\tau) = (w_1a^2\mathrm{e}^{-a\tau} + w_2b^2\mathrm{e}^{-b\tau}) - p^2\mathrm{e}^{-p\tau} . \tag{41}$$

In order to estimate how far the τ-axis should be extended in the numerical test calculations one can observe that $\exp(-\Gamma\tau)$ has decreased to approximately 1/100 of its initial value when τ has increased from 0 to $\tau_r = 4/\Gamma$. In the case of a binary distribution one then should select a value τ_r corresponding to the longest correlation time of interest, i.e. where the electric field correlation curve has reached the base line to within one per cent. If, for instance, $b < a$ one selects $\tau_r = 4/b$. Furthermore, the steps in τ could then be chosen to be $\Delta\tau = 1/(10b)$, which would give at least 40 values between 0 and τ_r. Finally, since it is only the ratio a/b that is of interest the test calculation can be performed according to a fairly simple scheme by varying this ratio for a fixed value of b.

Model Calculations for Explicit Laplace Transforms

For continuous distributions it is easy to find the correlation and deviation functions for distributions $\psi(\Gamma)$ such that the Laplace transform Ψ can be given in closed form. We will give results for two such distributions, normalized to 1, denoted Case III and Case IV below.

Case III. Let $u(t)$ denote the unit function defined as $u(t-a) = 1$ if $t > a$, otherwise $u = 0$. Then a normalized distribution can be defined according to

$$\psi(\Gamma) = [u(\Gamma - a) - u(\Gamma - b)]/(b - a) \qquad b > a\,, \tag{42}$$

where $\psi(\Gamma) = 1/(b-a)$ = const in the interval (a, b), otherwise $\psi(\Gamma) = 0$. It is easily shown that this corresponds to the Laplace transform

$$\Psi(\tau) = g(\tau) = (1/\tau)(e^{-a\tau} - e^{-b\tau})/(b - a) \qquad b > a \tag{43}$$

$$\langle\Gamma\rangle = (a + b)/2 = (a/2)(1 + b/a) \tag{44}$$

$$\omega(\tau) = g(\tau) - g_0(\tau) = (1/\tau)(e^{-a\tau} - e^{-b\tau})/(b - a) - \exp[-(a + b)\tau/2]\,. \tag{45}$$

Furthermore, the following characteristics apply to the distribution in question, cf. section 1:

$$\langle\Gamma^2\rangle = (b^2 + a^2 + ab)/3 \tag{44a}$$

$$\sigma^2 = (a - b)^2/12 \tag{44b}$$

$$\rho^2 = \sigma^2/\langle\Gamma\rangle^2 = (1/3)[(1 - b/a)/(1 + b/a)]^2\,. \tag{44c}$$

Case IV. Let k and a be real, positive numbers and define the distribution

$$\psi(\Gamma) = (a^{k+1}/k!)\Gamma^k e^{-a\Gamma}\,, \tag{46}$$

where $a^{k+1}/k!$ is a normalization factor. The corresponding Laplace transform is given by

$$\Psi(\tau) = g(\tau) = (a^{k+1}/k!)\Gamma_g(k+1)/(\tau+a)^{k+1}, \tag{47}$$

where $\Gamma_g(k+1)$ denotes the gamma function. If we limit ourselves to k being a positive integer, which we will do throughout this paper, Eq. (*47*) simplifies and we have

$$\Psi(\tau) = g(\tau) = a^{k+1}/(\tau+a)^{k+1} \tag{48}$$

$$\langle\Gamma\rangle = (k+1)/a \tag{49}$$

$$\omega(\tau) = g(\tau) - g_0(\tau) = a^{k+1}/(\tau+a)^{k+1} - \exp[-(k+1)\tau/a]. \tag{50}$$

Furthermore, if k is an integer the following characteristics apply to the distribution in question

$$\langle\Gamma^2\rangle = (k+1)(k+2)/a^2 \tag{49a}$$

$$\sigma^2 = \langle\Gamma^2\rangle/(k+1) = (k+1)/a^2 \tag{49b}$$

$$\rho^2 = \sigma^2/\langle\Gamma\rangle^2 = 1/(k+1). \tag{49c}$$

Comparison of Calculated Model Deviation Functions

Starting from the various expressions presented it is a straightforward task to calculate the deviation functions for a given distribution corresponding to a given $\langle\Gamma\rangle$ and various relative widths ρ^2. Obviously if the different cases, as presented above, are to be compared for similar values of $\langle\Gamma\rangle$ and ρ^2 then the appropriate equations relating $\langle\Gamma\rangle$ and ρ^2 to the parameters a, b, and k have to be solved.

Table I gives a summary of parameters used in the test calculations. Case IIA gives results for the mixture of two fractions with characteristic correlation times not too far apart (10 and 30, respectively, and one may think of these numbers being expressed in microseconds). Case IIB gives results for the mixture of two fractions with characteristic correlation times quite well separated (5 and 60, respectively). The deviation

TABLE I

Summary of data for calculated deviation functions; the quantities ρ^2 and $\langle\Gamma\rangle$ are calculated from the parameters a, b, and k, whereas ω_{max} has been read from the deviation plots

Case	ρ^2	$1/\langle\Gamma\rangle$	ω_{max}	w_1	a	b	k
IIA	0.302	23.1	0.050	0.15	1/10	1/30	–
	0.326	21.4	0.060	0.20			
	0.250	15	0.074	0.50			
	0.094	11.5	0.038	0.80			
	0.070	11.1	0.030	0.85			
IIB	2.196	22.6	0.263	0.15	1/5	1/60	–
	1.891	18.8	0.293	0.20			
	0.716	9.2	0.265	0.50			
	0.202	6.1	0.119	0.80			
	0.144	5.8	0.091	0.85			
IIC	0.062	37.5	0.018	0.50	1/30	1/50	–
III	0.250	20	0.080	–	1/150	14/150	–
III	0.320	20	0.106	–	1/500	1/10	–
IV	0.167	20	0.043	–	120	–	5
IV	0.250	20	0.063	–	80	–	3

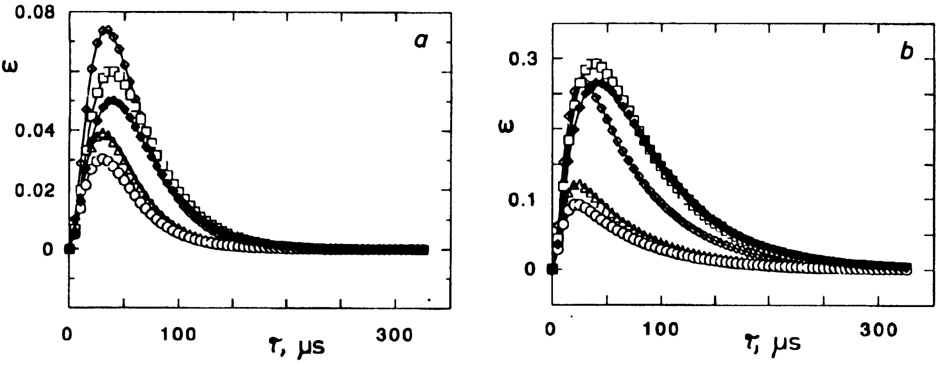

FIG. 1

Model deviation functions calculated for a mixture of two monodisperse fractions having *a* $\Gamma_1 = 1/10$, $\Gamma_2 = 1/30$ and *b* $\Gamma_1 = 1/5$, $\Gamma_2 = 1/60$ at different compositions (see Table I); ◊ $w_1 = 0.5$; ❐ 0.2; Δ 0.8; ○ 0.85; ◆ 0.15

functions for Case IIA is shown in Fig. 1*a*. Case IIB has similar deviation graphs (Fig. 1*b*) but the ordinate values are much larger. The maximum of the deviation function, ω_{max}, is plotted in Fig. 2*a* as a function of the relative composition w_1, i.e. the fraction of component 1 present, for IIA and IIB. Figure 2*a* shows that the function $\omega_{max}(w_1)$ passes a maximum. This maximum increases and its position shifts to lower values of w_1 as the difference in Γ increases. Furthermore, it can be inferred from Fig. 2*a* that if to a component a with a low characteristic correlation time (high diffusion coefficient, low molecular mass) there is added another component with higher characteristic correlation time (low diffusion coefficient, high molecular weight) there is a steady and fairly linear increase in ω_{max}, i.e. when w_1 is decreased from $w_1 = 1$ to a value closer to the maximum. A similar observation is made if to a component with a large characteristic correlation time there is added an increasing amount of a component with a small characteristic correlation time (component a), i.e. w_1 is increased from $w_1 = 0$ upwards towards the maximum. The largest values of ω_{max} may be expected when a fairly small amount of component a is added to the second component in the case of a high difference in correlation times. Thus for the mixture of fairly sharp fractions the deviation functions can be expected to give quite good information when one component is known to be dominant. The corresponding plot of ρ^2 against composition (Fig. 2*b*) behaves similarly to the plot in Fig. 2*a*. Hence, the relation between ω_{max} and the relative width, ρ^2, see Fig. 3, provides an approximately linear relation of some practical interest for continuous as well as bimodal samples as long as the relative width is not excessive (Cases IIA, III, and IV). The case with two widely differing species mixed together differs considerably from this picture, as indicated in Fig. 3.

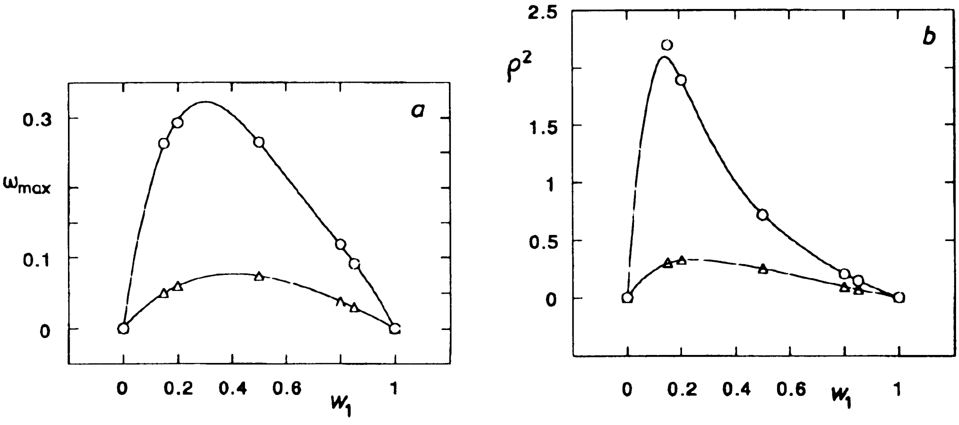

FIG. 2

The dependence of *a* maximum value of deviation and *b* relative width of the distribution on the composition of a mixture of two sharp fractions (see Table I); Δ $\Gamma_1 = 1/10$, $\Gamma_2 = 1/30$, and ○ $\Gamma_1 = 1/5$, $\Gamma_2 = 1/60$

Figures 4*a* and 4*b* give deviation functions for Case III and Case IV, respectively. Case III is a "pulse function" distribution, i.e. it has a constant, non-zero value in the interval (*a*, *b*), and it is clear that the deviation function – similar in shape to Case II – tends to tail out for longer correlation times more than in the bimodal case, cf. Fig. 1. The same is true for the continuous, single peaked function in Case IV. These two cases together with the bimodal distribution in Case II cover a fairly wide range of possible distributions met with in practice. The approximate coincidence of Cases IIA, III, and IV in Fig. 3 is not surprising. It reflects the low resolution[8,9] of the QELS technique to the detailed shape of the distributions having moderate widths. Thus, the empirical relationship between ω_{max} and ρ^2 (Fig. 3) would in all its approximation be useful for an estimation of the width of moderately broad distributions.

Experimental Deviation Plots

Table II summarizes the essential data from the experiments. In this table $\langle\Gamma\rangle$ has been obtained in the normal way from the experimental QELS correlation function. The maximum of the deviation function, ω_{max}, is read from the corresponding deviation function. The values of $(\rho^2)_{diag}$ have been taken from the approximate, empirical relationship in Fig. 3. The values of $(\rho^2)_{calc}$ have been calculated from the initial values of the first and second derivative of the correlation function with respect to τ. Clearly, the correct determination of deviations requires a precise determination of the initial slope, i.e. a sufficient number of points at low values of τ. At the same time the sum of two sufficiently different exponentials decays very slowly to zero and the experiment should be extended to large values of τ. This has not been possible with the correlator used (facility with 64 equidistantly spaced channels; as indicated earlier the computational method developed is also primarily intended for "non-separated" distributions). The requirement of sufficient precision of initial slope was preferred and therefore de-

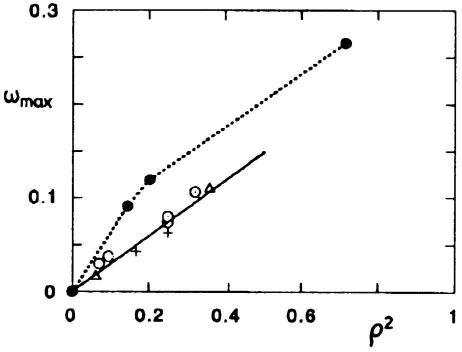

FIG. 3

The dependence of ω_{max} on relative width of the distribution in the case of high (dotted line, ●) and moderate polydispersity and/or Γ ratio for cases described in Table I; ○ IIA, Δ IIC, ⊙ III, + IV viation graphs were not obtained up to sufficiently high correlation times τ and could not be integrated to give the quantity $\langle \Gamma^{-1} \rangle$ according to Eq. (*18*). For a similar reason values of the distribution measure *m* according to Eq. (*27*) have not been calculated. The results with a nonlinear channel correlator (BI 8000) will be published in the near future.

It is clear from Table II that there is good agreement between $(\rho^2)_{\mathrm{diag}}$ and $(\rho^2)_{\mathrm{calc}}$. The results for PS 6 confirm a narrow fraction ($M_w/M_n \approx 1.06$) giving zero deviation within the experimental error. The other standard polystyrene (PS 5) is wider ($M_w/M_n \approx$

TABLE II

Summary of data from QELS experiments on polystyrene (PS) samples in toluene and polyethylene oxide (PEO) samples in water; the quantities $\langle \Gamma \rangle$, $\omega_{\max}$, $(\rho^2)_{\mathrm{diag}}$ and $(\rho^2)_{\mathrm{calc}}$ have been experimentally determined as described in the text

Experiment	$M_w \cdot 10^{-3}$	$1/\langle\Gamma\rangle$	$\omega_{\max}$	$(\rho^2)_{\mathrm{diag}}$	$(\rho^2)_{\mathrm{calc}}$
PS 5	1 800	122.2	0.067_6	0.27	0.23
PS 6	498	79.2	~0	~0	~0
PS 8	Mixture[a]	89.6	0.044_7	0.20	0.22
PS 13	295	58.9	0.091_5	0.30	0.40
PEO 17	150	303.5	0.295_5	0.8	0.9
PEO 19[b]	150	106.6	~0	~0	~0

[a] Mixture PS 5/PS 6 1 : 2 by weight; [b] PEO 17, aggregate component filtered off.

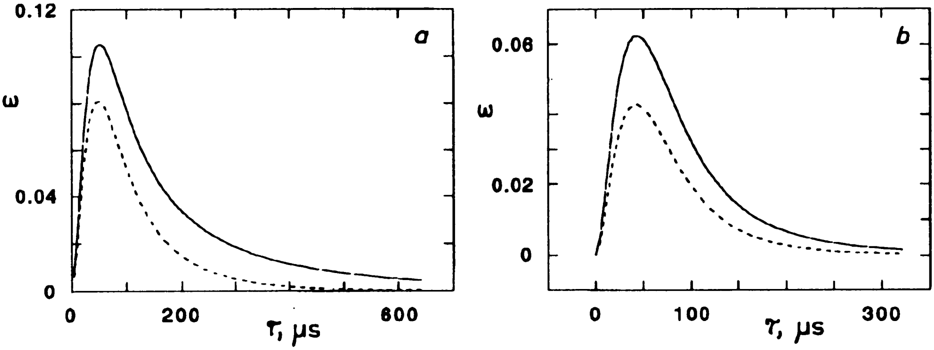

FIG. 4

Model deviation functions calculated *a* for a mixture of two rectangular pulse distributions having different widths: *b*/*a* = 14, *a* = 1/150 (dashed line) and *a*/*b* = 50, *a* = 1/500 (full drawn line), see Table I, and *b* for Schulz–Zimm distributions having different widths: *a* = 120, *k* = 5 (dashed line) and *a* = 80, *k* = 3 (full drawn line), see Table I

1.2) but the width itself cannot explain the observed non-zero deviation. The explanation may be found in the shape of the molar mass distribution. This polystyrene sample was shown[11] to have a long low molecular mass tail. This may be interpreted as a low amount of a component with a high diffusion constant and this is the case when a large ω_{max} should be expected. When this fraction is mixed with PS 6 in the ratio 1 : 2 by weight, it is almost sure that the maximum in the ω_{max} vs composition plot is passed (cf. Fig. 2*a*) and the observed ω_{max} goes down. The polystyrene sample PS 13 is known[7] to have a fairly broad molar mass distribution ($M_w/M_n \approx 5$) extended down to the oligomeric range. The values of ρ^2 (Table II) reflect the increased width of the distribution as seen in comparison with the value 0.22 found in the case of the mixture PS 5/PS 6.

The fairly low values of ω_{max} in all PS experiments again exemplify the low polydispersity resolution of the QELS technique. If it is assumed that $D \sim M^{-1/2}$, then one has for two monodisperse fractions $D_1/D_2 = (M_1/M_2)^{1/2} = \Gamma_1/\Gamma_2$. Hence to obtain the ratio $\Gamma_1/\Gamma_2 = 3$ (Case IIA) M_2/M_1 must be 9. The mixture PS 5/PS 6 ($M_2/M_1 \approx 3.6$) is easily resolved by size exclusion chromatography but gives $\Gamma_1/\Gamma_2 \sim 1.9$ which is near to Case IIC (Table I) where ω_{max} for a 1 : 1 mixture is only 0.02. Strictly speaking these values are valid for the theta-solvent behaviour[11] but the exponent in the $D \sim M^{-\alpha}$ relation increases only moderately with the solvent quality (in a good solvent like toluene[12] α = 0.57) and therefore this insensitivity must be regarded as a general feature of the technique.

If the sample contains two species sufficiently different in Γ as in the case of PEO 17 ($\Gamma_1/\Gamma_2 \sim 10$) in Fig. 6, a smooth ω-plot deploying a much higher maximum is obtained,

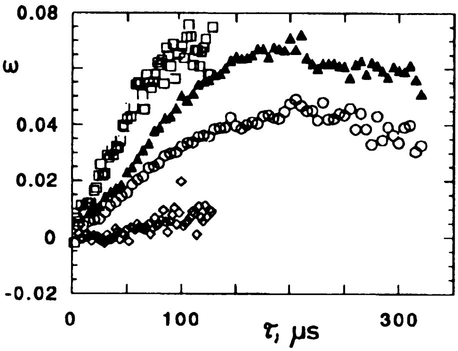

FIG. 5

Experimental deviation functions of different polystyrene samples described in Table II: ◊ PS 6, ▲ PS 5, ○ PS 8, □ PS 13

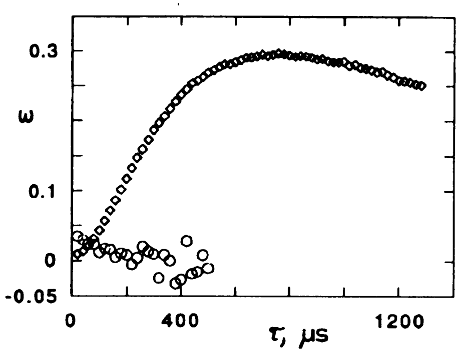

FIG. 6

Experimental deviation functions of polyethylene oxide (see Table II); ◊ before and ○ after removal of big particle component well comparable to that obtained in Case IIB (Table I). When the big particle component was filtered off the deviation dropped to zero due to a narrow molecular mass distribution of the sample itself.

It can be concluded that even if this procedure based on deviation functions cannot compete with other numerical inversion methods[2] for Eq. (7) in the determination of molecular size distributions it may substantially help to visualize the magnitude of the effect of polydispersity and as a prerequisite for a decision concerning how far it is meaningful to pursue more precise calculations. This is essentially equivalent to a judgement of the noise level of the experiment and of the "information content" to be expected.

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