

QELSS DIFFUSION DATA FOR MODERATELY BROAD MOLAR MASS DISTRIBUTION POLYMER SAMPLES COMPARED WITH DATA FROM CLASSICAL GRADIENT TECHNIQUES

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The differences between the QELSS and classical diffusion coefficient of a polydisperse polymer resulting from distinct definitions of experimentally accessible average values are calculated for two assumed specific forms of molar mass distributions. Predicted deviations are compared with the experiment using NBS 706 standard polystyrene. QELSS D_z of this sample relates within 2–4% to the classical diffusion coefficient, if the Schulz–Zimm molar mass distribution is assumed to be valid. In general, differences between the height-area and QELSS diffusion coefficient of about 20% may be found for $M_w/M_n \sim 2$, and this value may increase above 35%, if strongly tailing molar mass distribution pertains to the sample.

In a previous paper¹ it has been shown that QELSS and classical diffusion coefficients are equal within $\pm 2\%$ in the case of sharp polymer fractions, if QELSS experiments are performed in very dilute solution where the concentration dependence of D can be neglected. It has been found that the influence of a small polydispersity of the sample resulted only in a negative 2–3% error in the QELSS diffusion constant, if a single exponential fit instead of the second cumulant fit was used. Thus, the influence of different definition of the QELSS diffusion coefficient (D_z) was negligible in comparison with classical diffusion in the case of very sharp fractions.

For a polydisperse macromolecular solute a well-known equation holds² for the electric field autocorrelation function

$$|g^{(1)}(\tau)| = \int_0^\infty G(\gamma) \exp(-\gamma\tau) d\gamma, \quad (1)$$

where τ is the delay time, $\gamma = DK^2$, D and K being the diffusion coefficient and scattering vector, respectively. The single exponential is replaced by a normalized distribution of exponentials $G(\gamma)$ defined³ as the fraction of the total intensity scattered by molecules having γ within the interval $\gamma, \gamma + d\gamma$. In the case of classical

gradient diffusion, the binary diffusion equation⁴

$$\frac{dn}{dx} = \frac{\Delta n_0}{2\sqrt{(\pi Dt)}} \exp(-x^2/4Dt) \quad (2)$$

is replaced⁵ by the sum or distribution of gradient curves

$$\frac{dn}{dx} = \frac{\Delta n_0}{2\sqrt{(\pi t)}} \int_0^\infty F(D) D^{-1/2} \exp(-x^2/4Dt) dD. \quad (3)$$

Here, Δn_0 is the initial difference between the refractive indices of solution, x is the coordinate in the cell, t is time and $F(D)$ is the differential mass distribution function of diffusion coefficients, defined so that the product $F(D) dD$ gives the mass fraction of the polymer having the diffusion coefficient between D and $D + dD$. Clearly, the difference in definitions $G(\gamma)$ and $F(D)$ results in different average values of the diffusion coefficients determined using Eqs (1) and (3); this difference can no longer be neglected, if moderately broad or broad polydisperse samples are studied.

It is the aim of this paper to calculate these differences assuming two different specific forms of the molar mass distribution to see to what extent the comparison of the QELSS and classical diffusion coefficient can be made, depending on the width of the molar mass distribution. As an illustration, QELSS experiments on a moderately broad standard polystyrene sample have been performed, analyzed according to the principles outlined previously¹ specified for moderate polydispersity, and a comparison with classical diffusion data for the same sample is presented.

THEORETICAL

The same specific forms of molar mass distribution functions differing in the degree of asymmetry as in the previous paper¹ are used: (i) the Schulz-Zimm distribution in the form

$$f(M) = \frac{a^{b+1}}{\Gamma(b+1)} M^b \exp(-aM), \quad (4)$$

where $a, b > 0$ and Γ denotes the gamma function; the necessary width of the distribution is given as $M_w/M_n = 1 + 1/b$. (ii) Pearson's distribution

$$f(M) = \frac{\beta^{\varepsilon-1}}{\Gamma(\varepsilon-1)} M^{-\varepsilon} \exp(-\beta/M) \quad (5)$$

with $M_w/M_n = (\varepsilon - 1)/(\varepsilon - 2)$ and $\beta > 0, \varepsilon > 2$. The normalized mass distribution

$f(M) dM$ is defined as the mass fraction of molecules having M in the interval $M, M + dM$ and this is the distribution operating through $G(\gamma)$ and $F(D)$ in QELSS and classical diffusion, respectively. The intensity fraction in Eq. (1) is the generalized statistical weight⁶ defined in terms of z_i arguments as the z -fraction

$$Z_i = \frac{z_i}{\sum z_i} = \frac{w_i M_i}{\sum w_i M_i} = G(\gamma_i) = G(\gamma) d\gamma; \quad (6)$$

here, $z_i = w_i M_i = n_i M_i^2$, w_i , n_i being weights and numbers of molecules with M_i , respectively. From the z -defined distribution of $G(\gamma)$ the z -average follows as the first moment^{6,7}; using the necessary relation between $f(M)$ and $G(\gamma)$ following directly from their definition

$$G(\gamma) d\gamma = \frac{1}{M_w} M f(M) dM, \quad (7)$$

where M_w is the mass-average molar mass, we obtain

$$D_z = \frac{\gamma_z}{K^2} = \frac{1}{K^2} \int_0^\infty \gamma G(\gamma) d\gamma = \frac{\int_0^\infty DM f(M) dM}{\int_0^\infty M f(M) dM} \quad (8)$$

in agreement with². This is the only case where the "true z -average" according to Kinnell⁷ is available experimentally, and this is, of course, not equal to the "formal z -average" of D based on the mass distribution of diffusion coefficients due to the fact that an analogous relation to $z_i = w_i M_i = n_i M_i^2$ cannot be used⁶ in the case of the diffusion and sedimentation constant. We refer to Kinnell⁷, noting that only the "formal averages" are accessible experimentally in the classical diffusion and sedimentation.

In the gradient diffusion experiment the average height-area diffusion coefficient is determined⁴ in most cases by

$$D_1 = D_{HA} = \left[\int_0^\infty D^{-1/2} F(D) dD \right]^{-2}. \quad (9)$$

The polarization interferometer⁸ enables us to determine four different averages of the diffusion coefficient in polydisperse systems;

$$D_2 = \frac{\int_0^\infty D^{-1/2} F(D) dD}{\int_0^\infty D^{-3/2} F(D) dD} \quad (10)$$

is the most precise, the next one in precision being D_1 defined by Eq. (9).

To compare QELSS D_z with the averages defined by (9), (10), we use the relation

$$D = K_D M^{-\alpha}, \quad (11)$$

and, noting simply by definitions,

$$f(M) dM = -F(D) dD, \quad (12)$$

we get after some rearrangements the result

$$D_z = \frac{\int_0^\infty D^{(\alpha-1)/\alpha} F(D) dD}{\int_0^\infty D^{-1/\alpha} F(D) dD}. \quad (13)$$

In a special case of the Θ -solvent ($\alpha = 0.5$),

$$D_z = \frac{\int_0^\infty D^{-1} F(D) dD}{\int_0^\infty D^{-2} F(D) dD}. \quad (14)$$

For $\alpha = 2/3$ that corresponds to the exponent $k = 1$ in the viscosity dependence on molar mass $[\eta] \sim M^k$, if the Flory-Fox relation⁹ $k = 3\alpha - 1$ holds, we have from (13) that $D_z = D_2$ as defined by Eq. (10). Hence, in this case the classical D_2 value should be directly comparable with the QELSS D_z , independently of the polydispersity of the sample.

To get a comparison between D_z and D_1 , D_2 it is necessary to calculate the integrals in Eqs (9), (10) and (13). Using Eqs (4), (11), we get after some algebra and integrations for the Schulz-Zimm as a result in the terms of gamma functions

$$\frac{D_1}{D_z} = \frac{\Gamma(b+2) \Gamma^2(b+1)}{\Gamma^2[(2b+\alpha+2)/2] \Gamma(b-\alpha+2)} \quad (15)$$

and

$$\frac{D_2}{D_z} = \frac{\Gamma(b+2) \Gamma[(2b+\alpha+2)/2]}{\Gamma(b-\alpha+2) \Gamma[(2b+3\alpha+2)/2]}. \quad (16)$$

The same can be done using Eqs (5), (11), (9), (10) and (13) for Pearson's case

$$\frac{D_1}{D_z} = \frac{\Gamma(\varepsilon-2) \Gamma^2(\varepsilon-1)}{\Gamma^2[(2\varepsilon-\alpha-2)/2] \Gamma(\alpha+\varepsilon-2)} \quad (17)$$

and

$$\frac{D_2}{D_z} = \frac{\Gamma(\varepsilon-2) \Gamma[(2\varepsilon-\alpha-2)/2]}{\Gamma(\alpha+\varepsilon-2) \Gamma[(2\varepsilon-3\alpha-2)/2]}. \quad (18)$$

EXPERIMENTAL

A standard polystyrene sample NBS 706 was characterized (NBS certificate) by $M_n = 136\,500$, $M_w = 216\,000$, $M_w = 257\,800$ (light scattering), $M_w = 288\,100$ (sedimentation equilibrium). Solutions in toluene were prepared by weighing.

A QELSS experimental setup, filtration of solutions and evaluation procedure were described in a previous paper¹. Classical diffusion experiments and calculation procedures were described in literature^{5,10}.

RESULTS AND DISCUSSION

The calculated ratios of the diffusion coefficients D_1/D_z and D_2/D_z to the distribution width up to $M_w/M_n = 11$ are plotted in Fig. 1a for the Schulz-Zimm case (Eqs (15), (16)) and in Fig. 1b for the Pearson distribution (Eqs (17), (18)). We note only a small change in D_2/D_z above $M_w/M_n \sim 3$ and in D_1/D_z above $M_w/M_n \sim 5$ for the Schulz-Zimm function. Nevertheless, comparing D_1 with D_z , we achieve a difference of about 25% above $M_w/M_n = 3$. The influence of greater asymmetry of the distribution results in much higher values of D_i/D_z for the Pearson case. Also, we see that the highest difference between D_2 and D_z is found in the Θ -solvent; the opposite is true for D_1 .

The corresponding plot for polystyrene-toluene ($\alpha = 0.57$) is in Fig. 2 for both distributions in the interval $M_w/M_n \leq 3$ found previously¹ as a reasonable limit of

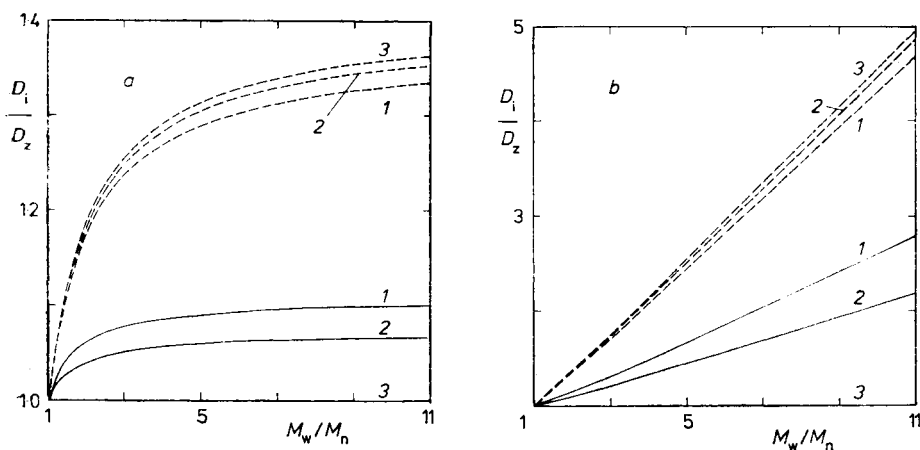


FIG. 1

The dependence of the ratios of diffusion coefficients D_1/D_z (broken lines) and D_2/D_z (solid lines) on the width of the Schulz-Zimm (a) and Pearson (b) molar mass distribution. Values of α : 1.050, 2.057, 3.067

applicability of the cumulant evaluation procedure. There is almost no difference between the influence of the shape of distribution below $M_w/M_n = 1.25$. The values of $D_1/D_z = 1.07$, $D_2/D_z = 1.015$ for the Schulz-Zimm and 1.085, 1.017 for Pearson's case, respectively, indicate that the difference between the classical and QELSS diffusion should be detectable using the height-area diffusion coefficient, if the precision of both diffusion methods approaches $\pm 2\%$. Bryngdahl's interferometer value of D_2 remains directly comparable within this precision. Let us note that $M_w/M_n \sim 1.25$ is the upper limit of the distribution width of some polymer standards with higher molar masses.

A set of experiments with the NBS standard sample was measured at the concentration 0.0557 wt. %. Two different sampling times $\Delta\tau$ were used to check the attainment of baseline. These data were evaluated according to the procedure described in the previous paper¹. The maximum channel numbers j_{\max} for a 2% error using the 2nd order approximation (Fig. 5, ref.¹) were calculated $j_{\max} = 20, 22$ for the Schulz-Zimm and Pearson's case, respectively, using $\Delta\tau = 2 \cdot 10^{-6}$. For $\Delta\tau = 5 \cdot 10^{-6}$

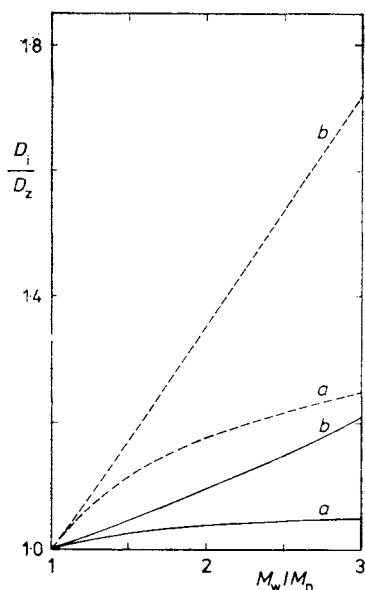


FIG. 2

Calculated ratios of diffusion coefficients D_1/D_z (broken lines) and D_2/D_z (solid lines) for the system polystyrene-toluene ($\alpha = 0.57$). Molar mass distribution according to Schulz-Zimm (a) and Pearson (b)

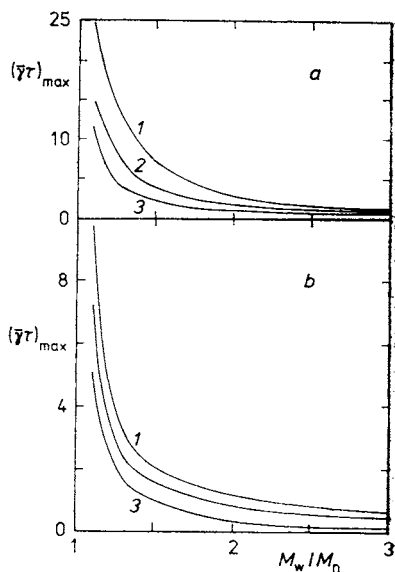


FIG. 3

Condition of applicability of the 3rd order cumulant fit with 2% error. Molar mass distributions according to Pearson (a) and Schulz-Zimm (b). Values of α : 1.05, 2.057, 3.067

only nine channels remained below the 2% limit. To extend the number of usable channels with a 2% error, the conditions of applicability of the third order cumulant approximation may be written

$$0.02[1 - R(\bar{y}\tau) + Q(\bar{y}\tau)^2] \geq S(\bar{y}\tau)^3. \quad (19)$$

We refer to the previous paper¹ for details. The resulting values of $(\bar{y}\tau)_{\max}$ against M_w/M_n for both distributions are plotted in Fig. 3 and calculated $j_{\max} = 23, 48$ correspond to $\Delta\tau = 2 \cdot 10^{-6}$ for the Schulz-Zimm and Pearson's function, respectively. The detailed shape of distribution is seldom known; therefore, we cannot safely use Pearson's case and gain only two more channels, but the expected advantage re-

TABLE I

QELSS results for standard polystyrene NBS 706. Conditions: $\Delta\tau = 2 \cdot 10^{-6}$ s, average counting rate 177 000 c/s, 21.7°C, $c = 0.0557$ wt. %, statistical baseline. Symbols are defined in the text (D_z in $\text{cm}^2 \text{s}^{-1}$)

No. of experiment	2nd degree		3rd degree		ΔB %
	$D_z \cdot 10^7$	K_2/K_1^2	$D_z \cdot 10^7$	K_2/K_1^2	
1	2.625	0.20	2.697	0.37	0.01
2	2.542	0.15	2.660	0.44	0.05
3	2.640	0.22	2.634	0.24	0.02
4	2.580	0.20	2.605	0.29	0.06
<i>Average D_z</i>	2.597		2.649		
<i>Corr. to 25°C</i>	2.732		2.787		

TABLE II

Comparison of QELSS $D_z = 2.787 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ with classical diffusion coefficients at 25°C for polystyrene NBS 706

Description		$D_1 \cdot 10^7$ $\text{cm}^2 \text{ s}^{-1}$	$D_2 \cdot 10^7$ $\text{cm}^2 \text{ s}^{-1}$	D_1/D_z	D_2/D_z
Measured	ref. ⁵	3.384	2.966	1.21	1.06
	ref. ¹⁰	—	2.902	—	1.04
Calculated	Schulz-Zimm	3.288	2.901	1.18	1.04
	Pearson	3.762	3.066	1.35	1.10

sulting from the third order fit is a better precision of the first cumulant and, hence, of the D_z value.

The results of calculations are summarized in Table I. We see that the reproducibility of D_z in a single experiment is about $\pm 2\%$ and a 2% difference between the 2nd and 3rd order fit. The 3rd order cumulant fit is believed to have a lower error in D_z and is used for further comparison. We see also reasonable values of the second cumulant, although higher for the 3rd order fit, noting that the error estimate of the K_2 value runs from $\pm 15\%$ up to $\pm 64\%$. Experiments with $\Delta\tau = 5 \cdot 10^{-6}$ (not included in the table) gave the same baseline difference ΔB as with $\Delta\tau = 2 \cdot 10^{-6}$, thus confirming the correct choice of this value. All data were also evaluated using the average baseline from the last eight delayed channels for comparison with the statistical baseline. A slightly higher D_z values were found with the average difference fairly below the requested 2% error, but a higher scatter, less reliable cumulant values and sometimes overfitting (using the 3rd order fit) are noticed. Hence, the statistical baseline, apparently more precise, was preferred.

The comparison of QELSS D_z with the classical diffusion coefficients is presented in Table II. The certified values of the sample used give $M_w/M_n = 1.89$, if the light scattering M_w is used, but with M_w from the sedimentation equilibrium $M_w/M_n = 2.11$ is found. Due to our experience, the sedimentation equilibrium value is believed to be at least comparable in precision with light scattering. This is also supported by NBS fractionation data¹¹ ($M_w/M_n = 2.1$, $M_z/M_w = 1.38$). Therefore, an average $M_w/M_n = 2.0$ was used to find the calculated ratios D_i/D_z for both distributions used. One can see from Table II that the D_z value relates to both classical diffusion within 2–4% in the case of Schulz-Zimm, thus confirming the applicability of this function with $b = 1$, i.e., the most probable distribution¹², to this sample.

Summarizing, we cannot expect direct agreement between classical and QELSS diffusion data for samples of moderate polydispersity. In the case of $M_w/M_n \sim 2$ we may obtain differences of about 20% between the height-area and QELSS diffusion coefficient, and this difference may increase up to 35%, if a strongly tailing distribution of molecular mass pertains to the sample.

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