Influence of Polydispersity on the Dynamic Structure Factor of Macromolecules in Dilute Solution

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Received March 26, 1999; Revised Manuscript Received July 7, 1999

ABSTRACT: The influence of polydispersity on the dynamic structure factor of macromolecules in dilute solution is investigated. Analytical expressions are derived for the translational diffusion coefficient. It is found that the translational diffusion coefficient is less influenced by polydispersity than the mean square radius of gyration. Moreover, the shape of the dynamic structure factor at various scattering vectors is investigated. For a polydisperse macromolecular solution the dynamic structure factor is not a single-exponential function at small scattering vectors. The first cumulant of the dynamic structure factor is compared with dynamic light scattering measurements on polydisperse polysaccharides in dilute solution. Our theoretical calculations agree well with experimental data.

1. Introduction

Dynamic light scattering from macromolecules in dilute solution is a well-established and useful technique for investigating the translational and internal motion of such molecules. A problem of the scattering curve analysis results from polydispersity of the scattering system, which plays an important role for supermolecular structures. Most of the theoretical studies have focused on monodisperse macromolecular solutions.[1−5] The theory of the dynamic structure factor of polydisperse macromolecular solutions is much less developed. Up to now only the small scattering vector regime has been considered theoretically.[6−10] In the present paper we calculate the dynamic structure factor for dilute polydisperse macromolecular solutions in the whole scattering vector range and compare these results with experimental data. Our theoretical approach for the dynamic structure factor of monodisperse macromolecular solutions which has been successfully applied to quasielastic neutron and dynamic light scattering measurements on various macromolecules and wormlike micelles[5,11−14] is chosen as the basis of our present calculations.

2. Theory of Dynamic Structure Factor

In general, for a dilute solution containing macromolecules of different molecular weight the dynamic structure factor is given by the *z*-average[2]

$$\langle S(\mathbf{q},t)\rangle_z = \frac{\int_0^\infty \mathrm{d}L\; w(L) L S(\mathbf{q},L,t)}{\int_0^\infty \mathrm{d}L\; w(L) L} \qquad (2.1)$$

where $w(L)\,\mathrm{d}L$ is the fraction of macromolecules with contour length between L and $L + \mathrm{d}L$. $S(\mathbf{q},L,t)$ is the dynamic structure factor for a dilute solution of identical macromolecules of contour length L. Thus, the dynamic structure factor for polydisperse macromolecular solutions has to be calculated as a function of contour length and the result then averaged over the distribution $w(L)L$. There are various well-known length distributions such as the Schulz−Zimm distribution,[15,16] the log-normal distribution,[17] and the Tung distribution.[18] The Schulz−Zimm distribution applies for the polymerization kinetics and reads

$$w(L) = \frac{L^m}{\Gamma(m+1)}\left(\frac{m+1}{L_\mathrm{w}}\right)^{m+1} \exp\left(-\frac{(m+1)L}{L_\mathrm{w}}\right) \qquad (2.2)$$

with

$$\frac{1}{m} = \frac{L_\mathrm{w}}{L_\mathrm{n}} - 1 \qquad (2.3)$$

and

$$L_\mathrm{w} = \int_0^\infty \mathrm{d}L\; w(L)L \qquad (2.4)$$

L_w and L_n are the weight-average and number-average contour lengths, respectively. Γ is the Gamma function. Varying m from ∞ to 0 changes the distribution from monodisperse to infinitely broad. Figure 1 displays $w(L)L$ calculated according to eq 2.2 for three different polydispersities $L_\mathrm{w}/L_\mathrm{n} = 1.5, 2, 5$. From the figure and eq 2.1 it follows that for polydisperse solutions with a broad length distribution ($L_\mathrm{w}/L_\mathrm{n} = 5$) even macromolecules with contour lengths larger than three times the weight-average contour length contribute significantly to the dynamic structure factor. Thus, a theoretical investigation of the dynamic structure factor for polydisperse macromolecular solutions requires a chain model which captures the dynamic properties of macromolecules of different contour lengths and hence of different stiffnesses. Recently, we investigated analytically the dynamical properties of linear macromolecules with any degree of molecular stiffness in dilute solution.[5,11−14]

In our calculations a polymer chain of contour length L and persistence length $1/(2p)$ is represented as a continuous, differentiable space curve $\mathbf{r}(s,t)$, where s indicates distances along the chain. The persistence length characterizes the molecular stiffness. Equilibrium properties of our chain model, like the mean square radius of gyration and the mean square end-to-end distance, are identical with those of the Kratky−Porod wormlike chain.[12] The major advantage of our approach is that it allows us to investigate the dynamics of

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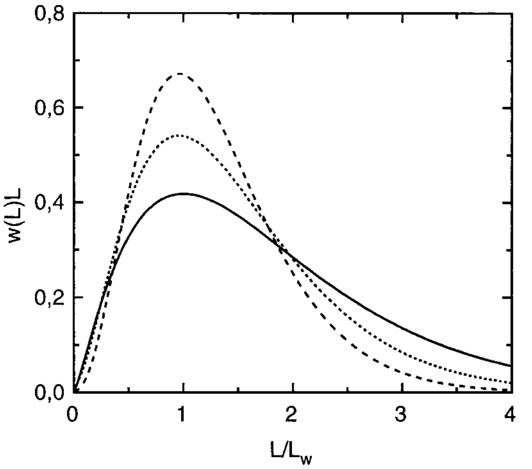

Figure 1. Schulz−Zimm distribution $w(L)L$ for three different polydispersities (dashed line, $L_w/L_n = 1.5$; short dashed line, $L_w/L_n = 2$; solid line, $L_w/L_n = 5$). The curves are calculated according to eq 2.2.

macromolecules with any degree of stiffness. In particular, a detailed comparison of our theoretical results with dynamic light scattering experiments on monodisperse DNA of different contour lengths exhibits good agreement.[5,12] Consequently, we study in the following the dynamics of polydisperse macromolecular solutions in terms of our previous model calculations for $S(\mathbf{q},L,t)$ and eq 2.1.

According to our theoretical approach presented in ref 5 the dynamic structure factor $S(\mathbf{q},L,t)$ for a dilute solution of identical semiflexible macromolecules is given by ($q = |\mathbf{q}|$)

$$S(\mathbf{q},L,t) = \frac{e^{-q^2D(L)t}}{L^2}\int_{-L/2}^{L/2}\int_{-L/2}^{L/2} \mathrm{d}s\,\mathrm{d}s'\,\exp\left(-\frac{q^2}{6}a(s-s')\right)\times \exp\left(-\frac{q^2k_BT}{3\pi\eta}\sum_{l=1}^{\infty}\tau_l\psi_l(s')\left(1-\exp\left(-\frac{t}{\tilde{\tau}_l}\right)\right)\right) \quad (2.5)$$

with the mean square internal distance

$$a(s-s') = \langle(\mathbf{r}(s,t)-\mathbf{r}(s',t))^2\rangle = \frac{|s-s'|}{p} - \frac{1}{2p^2}(1-e^{-2p|s-s'|}) \quad (2.6)$$

and the relaxation times $\tilde{\tau}_l$

$$\frac{\tau_l}{\tilde{\tau}_l} = 1 + \sqrt{\frac{3}{2\pi}}\int_{-L/2}^{L/2}\int_{-L/2}^{L/2}\mathrm{d}s\,\mathrm{d}s'\,\frac{\psi_l(s)\psi_l(s')}{\sqrt{a(s-s')}}\exp\left(-\frac{3d^2}{2a(s-s')}\right) \quad (2.7)$$

The translational diffusion coefficient of the macromolecules is given by

$$D(L) = \frac{k_BT}{3\pi\eta L}\left(1+\frac{\sqrt{6}}{\sqrt{\pi}L}\int_d^L \mathrm{d}s\,\frac{(L-\mathrm{s})}{\sqrt{a(s)}}\exp\left(-\frac{3d^2}{2a(s)}\right)\right) \quad (2.8)$$

where d is the hydrodynamic diameter of the macromolecules. The temperature (T) and viscosity (η) characterize the solvent. $\psi_l(s)$ are the eigenfunctions (eqs 2.22−2.24 of ref 5) of the normal-mode analysis describing the intramolecular dynamics. The corresponding eigenvalues are characterized by the relaxation times τ_l. Our model yields a crossover from intramolecular Rouse to bending modes with increasing mode number l on small length scales even for very flexible macromolecules due to molecular stiffness. The relaxation times of the bending modes are proportional to L^4 and exhibit the dependence $(2l-1)^{-4}$ on the mode number, as known for the weakly bending rod model of Aragón and Pecora.[19] The first relaxation time τ_1 exhibits for very flexible macromolecules the typical Rouse behavior, whereas for stiff macromolecules the well-known relation $\tau_1 \sim L^3$ is found. The hydrodynamic interaction is included in the study of the intramolecular dynamics of our model in terms of the relaxation times $\tilde{\tau}_l$ which are calculated using the Rotne−Prager tensor.[20] The influence of the hydrodynamic interaction on the relaxation times for semiflexible macromolecules becomes more important with both increasing chain flexibility and increasing mode number l. In evaluating the dynamic structure factor according to eq 2.5 we found that for scattering vectors larger than the inverse persistence length the stiffness of the macromolecules is important for any kind of macromolecule, i.e., even for very flexible ones. Both the shape of the dynamic structure factor and the initial decay rate of the dynamic structure factor differ from the results known for flexible macromolecules. In particular we found a slower relaxation of the dynamic structure factor and weaker q-dependence of the initial decay rate, as is predicted by the Rouse−Zimm model for flexible macromolecules. For more details concerning our model calculations and a comparison with experimental data, the reader is referred to refs 5 and 11−14.

3. Diffusion Coefficient

In the regime of small scattering vectors the initial decay rate of the dynamic structure factor for polydisperse macromolecular solutions is characterized by the z-average translational diffusion coefficient

$$\langle D\rangle_z = -\lim_{t\to 0}\frac{d}{dt}\frac{\ln\langle S(\mathbf{q},t)\rangle_z}{q^2} = \frac{\int_0^\infty \mathrm{d}L\; w(L)LD(L)}{\int_0^\infty \mathrm{d}L\; w(L)L} \quad (3.1)$$

Although this formula can be evaluated numerically, characteristic features of the translational diffusion coefficient can be obtained from analytical approximations. To evaluate the integral over s in eq 2.8, the function $a(s)$ is divided into two regions which intersect at a contour coordinate s,

$$a(s) = \frac{|s|}{p} \quad (3.2)$$

where $s > 1/(2p)$, and

$$a(s) = s^2 \quad (3.3)$$

where $s < 1/(2p)$. In the region of eq 3.2 the function $a(s)$ is the mean square internal distance predicted for a random coil. On spatial scales smaller than the persistence length $a(s)$ exhibits rigid rod behavior (eq 3.3). In the limit of very flexible macromolecules (pL_w large) the translational diffusion coefficient reads with

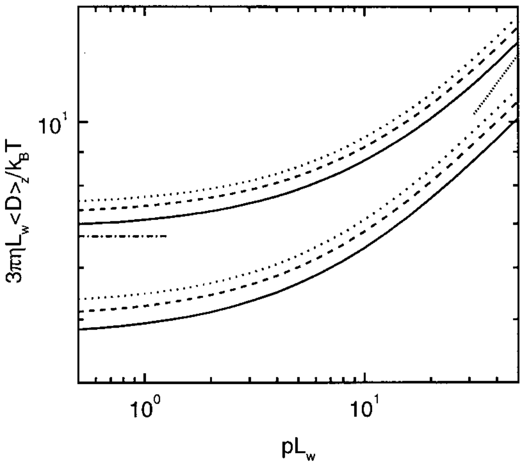

Figure 2. Translational diffusion coefficient numerically calculated using eq 3.1 and eq 2.2 for three different polydispersities (dotted lines, $L_w/L_n = 1$; dashed lines, $L_w/L_n = 1.5$; solid lines, $L_w/L_n = 5$). The lateral diameter (d) was fixed to $L_w/d = 500$ for the upper curves. In computing the lower three curves the ratio $L_w/d = 100$ was kept constant. The short dotted and the dashed dotted lines are calculated for $L_w/d = 500$ and $L_w/L_n = 5$ via eqs 3.4 and 3.5, respectively.

eq 3.2 and the Schulz–Zimm distribution (eq 2.2)

$$\langle D\rangle_z = \frac{k_BT}{3\pi\eta L_w}\left(1 + 8\sqrt{\frac{pL_w}{6\pi}\frac{\Gamma(m+1.5)}{\Gamma(m+1)\sqrt{m+1}}}\right) \quad (3.4)$$

In the opposite limit of rather stiff macromolecules (pL_w small) the translational diffusion coefficient reads with eqs 2.2 and eq 3.3

$$\langle D\rangle_z = \frac{k_BT}{3\pi\eta L_w}\left(1 + \sqrt{\frac{6}{\pi}}\left(\Psi(1+m) - 1 - \ln\left(\frac{(m+1)d}{L_w}\right)\right)\right) \quad (3.5)$$

where Ψ is the digamma function, i.e., the logarithmic derivative of the gamma function given by

$$\Psi(z) = \frac{\mathrm{d}}{\mathrm{d}z}\ln(\Gamma(z)) \quad (3.6)$$

Figure 2 displays the translational diffusion coefficient for different polydispersities. The crossover from the weight-average contour length dependence $\langle D\rangle_z \sim 1/\sqrt{L_w}$ for flexible macromolecules to $\langle D\rangle_z \sim \ln L_w/L_w + \mathrm{const}/L_w$ for stiff macromolecules is evident from the figure. Furthermore, the translational diffusion coefficient depends severely on the lateral diameter d. The influence of polydispersity on the translational diffusion coefficient is smaller than on the mean square radius of gyration given by[9,21]

$$\langle r_g^{\,2}\rangle_z = \frac{\int_0^\infty \mathrm{d}L\, w(L)L r_g^{\,2}(L)}{\int_0^\infty \mathrm{d}L\, w(L)L} = \frac{L_w}{6\pi}\frac{m+2}{m+1} - \frac{1}{4p^2} + \frac{1}{4p^3L_w} - \frac{m+1}{8mp^4L_w^{\,2}}\left(1 - \frac{(m+1)^m L_w^{\,m}}{(m+1+2pL_w)^m}\right) \quad (3.7)$$

with

$$r_g^{\,2}(L) = \frac{L}{6p} - \frac{1}{4p^2} + \frac{1}{4p^3L} - \frac{1-\mathrm{e}^{-2pL}}{8p^4L^2} \quad (3.8)$$

In particular, the computed translational diffusion coefficient for a polydisperse solution with $L_w/L_n = 1.5$ differs by less than 5% from the translational diffusion coefficient for a monodisperse solution ($L_w/L_n = 1$) for the molecular parameters considered in Figure 2. For the mean square radius of gyration (eq 3.7) a similar comparison yields a difference of about 16–32% ($pL_w = 0.5$:16% difference, $pL_w = 50$:32% difference). Hence, the translational diffusion coefficient is less influenced by polydispersity than the mean square radius of gyration.

4. Dynamic Structure Factor and Cumulant Expansion

For scattering vectors larger than the inverse radius of gyration, internal modes become essential and must be taken into account explicitly (eq 2.5). In Figure 3 we present a set of normalized dynamic structure factors as a function of t for polydisperse macromolecular solutions at two scattering vectors. The weight-average contour length L_w and the lateral diameter d were fixed to $L_w = 600$ nm and $d = 2.5$ nm. The persistence length is $1/2p = 100$ and 25 nm for the chains considered in part A and B of Figure 3, respectively. From the figure it is apparent that the influence of the polydispersity on the shape of the dynamic structure factor becomes less important with increasing scattering vector. The dynamic structure factor at scattering vector $q = 0.035$ nm^{-1} for a monodisperse solution is close to that for a polydisperse solution with $L_w/L_n = 1.5$. At this large scattering vector only short sections of the macromolecules are probed in the scattering experiment. Therefore the dynamic structure is rather independent of contour length and polydispersity. Most striking is the shape of the dynamic structure factor for polydisperse solutions at the small scattering vector $q = 0.005$ nm^{-1}, which exhibits a strong upturn in comparison with the single-exponential function for a monodisperse solution. The calculations reveal a shape whose decay rate is characteristic of a contour length larger than L_w. As pointed out earlier and obvious from Figure 1 macromolecules with contour lengths larger than the weight-average contour length L_w contribute significantly to the dynamic structure factor. Our calculations reveal that the dynamic structure factor for polydisperse macromolecular solutions is not a single exponential function at small scattering vectors and cannot be described by the translational diffusion coefficient only. The strong upturn of the dynamic structure factor in comparison with the single exponential function has been observed experimentally for polydisperse polysaccharides.[22,23] Moreover, a comparison of part A and B of Figure 3 exhibits a slower relaxation of the dynamic structure factor at small scattering vectors with increasing molecular stiffness.

In dynamic light scattering experiments commonly a cumulant fit of the dynamic structure factor is carried out to describe experimental data by

$$\ln\frac{\langle S(\mathbf{q},t)\rangle_z}{\langle S(\mathbf{q},0)\rangle_z} = -\Omega_z(\mathbf{q})t + \Omega_{z,2}(\mathbf{q})\frac{t^2}{2} - \ldots \quad (4.1)$$

$\Omega_z(\mathbf{q})$ and $\Omega_{z,2}(\mathbf{q})$ are the first and the second cumulants, respectively. In the regime of small scattering

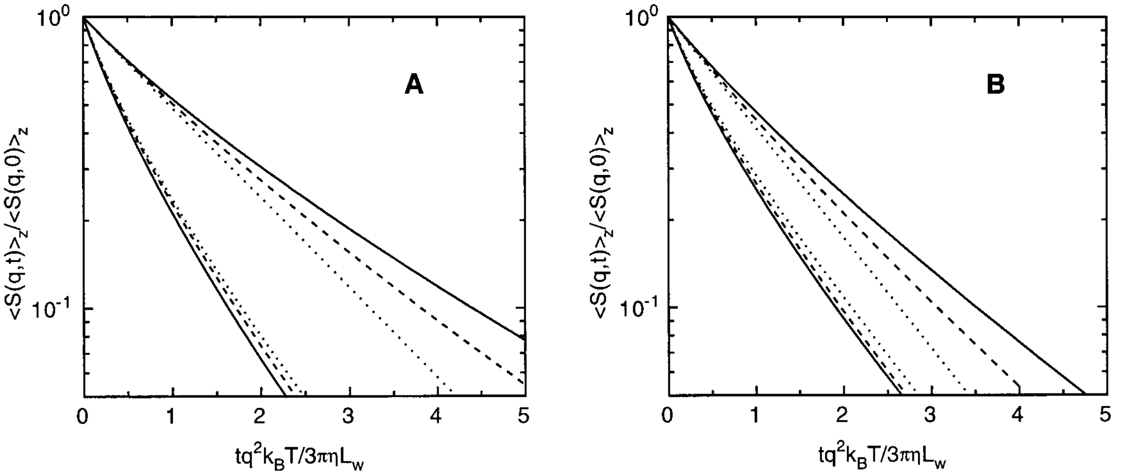

Figure 3. Normalized dynamic structure factors for polydisperse macromolecular solutions at two scattering vectors ($q = 0.005$ nm^{-1}: upper curves, 0.035 nm^{-1}: lower curves) calculated according to eqs 2.1 and eq 2.2 (dotted lines, $L_w/L_n = 1$; dashed lines, $L_w/L_n = 1.5$; solid lines, $L_w/L_n = 5$). The weight-average contour length L_w and the lateral diameter d were fixed to $L_w = 600$ nm and $d = 2.5$ nm. The persistence length is given by $1/2p = 100$ nm (A) and $1/2p = 25$ nm (B).

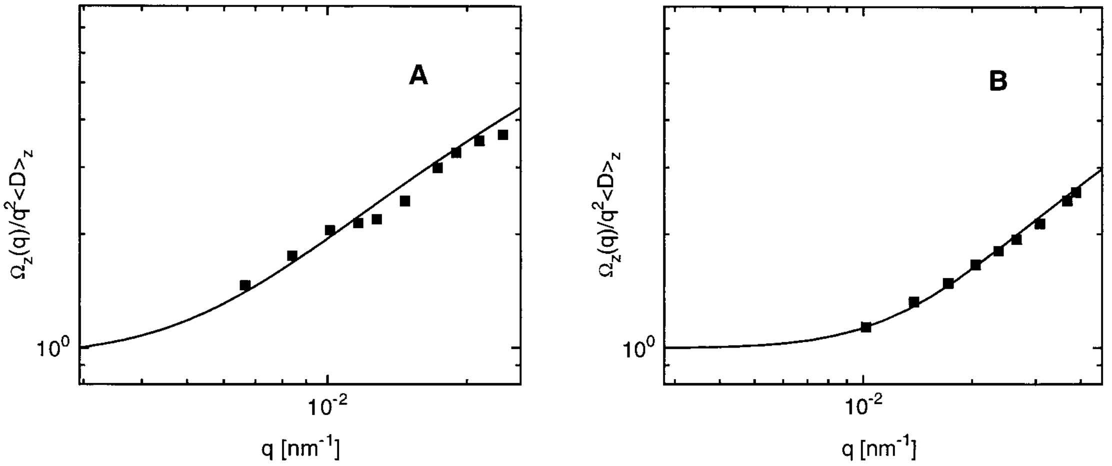

Figure 4. Normalized first cumulant of the dynamic structure factor for a polydisperse solution ($L_w/L_n = 2$) of semiflexible macromolecules. The weight-average contour length L_w and the persistence length $1/(2p)$ are given by (A) $L_w = 1609$ nm, $1/(2p) = 128$ nm; (B) $L_w = 517$ nm, $1/(2p) = 62$ nm. The squares display experimental data on the bacterial polysaccharide xanthan (A) and on the exocellular microbial polysaccharide from *R. trifolii strain* (B) in dilute solution.[22,25]

vectors the first cumulant is given by

$$\Omega_z(\mathbf{q}) = q^2\langle D\rangle_z \tag{4.2}$$

General aspects of cumulant expansions of the dynamic structure factor have been discussed by Koppel.[24] The number of terms of the cumulant expansion depends on the scattering vector range as well as the time range. Our calculations exhibit that a third-order cumulant fit of the dynamic structure factor for polydisperse macromolecular solutions yields sufficiently accurate estimations (deviations smaller than 1%) of $\Omega_z(\mathbf{q})$ if the time range is restricted to values where $\langle S(\mathbf{q},t)\rangle_z/\langle S(\mathbf{q},0)\rangle_z$ decays approximately to 0.8 of its original value. When the time range is increased, the deviations between the third cumulant fit and the full shape function increase. The criterion is that $\Omega_z(\mathbf{q})$ should become insensitive to the additional terms in the expansion. In general, an nth-oder cumulant fit of the dynamic structure factor for polydisperse macromolecular solutions always underestimates $\Omega_z(\mathbf{q})$. $\Omega_z(\mathbf{q})$ can be extracted from the dynamic structure factor data with reasonable accuracy if the time range is sufficiently small. However, if the purpose is also to investigate the shape of the dynamic structure factor as a function of time in order to extract information on polydispersity and molecular parameters, the time range of scattering measurements should be extended as much as possible, provided the experimental data are above the noise level.

5. Comparison with Experimental Results

Finally, we compare our model calculations for $\Omega_z(\mathbf{q})$ with experimental results of dynamic light scattering experiments on polysaccharides.[22,25] With the parameters characterizing the solvent, i.e., temperature (T) and viscosity (η), and the molecular parameters, i.e., weight-average contour length (L_w), persistence length [$1/(2p)$], and lateral diameter (d), we calculate the dynamic structure factor according to eq 2.1 and determine the first cumulant. A Schulz–Zimm length distribution with $L_w/L_n = 2$ is used, in agreement with the predictions in refs 22 and 25. The first cumulant together with experimental results for the bacterial polysaccharide xanthan[22] and the exocellular microbial polysaccharide from *Rhizobium trifolii strain* (TA-1-EPS)[25] are shown in Figure 4. The figure exhibits good agreement between our theoretical results and the experimental measurements. At scattering vectors larger than the inverse radius of gyration the relation $\Omega_z(\mathbf{q}) \sim q^\alpha$ with $\alpha = 2.7$ for TA-1-EPS ($pL_w = 4.14$) and $\alpha = 2.8$ for xanthan ($pL_w = 6.29$) is approximately valid. These q-dependencies differ from the exponent $\alpha = 3$ predicted by the Rouse−Zimm model for very flexible macromolecules.[4] Moreover, neither a rigid-rod model[26] nor sliding-rod model[27] account for the observed dependencies (cf. Figure 10 of ref 22 and Figure 13 of ref 25). The observed weaker q-dependencies of $\Omega_z(\mathbf{q})$ than predicted by the Rouse−Zimm model are mainly due to molecular stiffness. Only a small effect of polydispersity on the exponent α is found. Thus, studying the first cumulant of the dynamic structure factor at large scattering vectors can help to extract the persistence length of the macromolecules. The influence of the polydispersity becomes more pronounced if the shape of the dynamic structure factor is investigated.

6. Conclusion

We conclude that polydispersity influences the dynamic structure factor mainly at small scattering vectors and large times. In particular, the dynamic structure factor for polydisperse macromolecular solutions is not a single-exponential function at small scattering vectors and cannot be described by the translational diffusion coefficient only. At large scattering vectors, $q\sqrt{\langle r_g^2\rangle_z} \gg 1$, our calculations exhibit only a small influence of polydispersity on the first cumulant of the dynamic structure factor. With increasing molecular stiffness, a slower relaxation of the dynamic structure factor and a weaker scattering vector dependence of the first cumulant of the dynamic structure factor was found. A comparison of our theoretical calculations with dynamic light scattering experiments on polydisperse polysaccharides in dilute solution reveals good agreement.

Acknowledgment. This investigation is part of a project of the Sonderforschungbereich 239. The support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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MA990450F