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Remarks on the Interpretation of Dynamic Light Scattering from Gellan in Dilute Solution

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ABSTRACT: The dynamic structure factor of semiflexible macromolecules in solution is briefly discussed. Particularly, the theoretical calculations are compared with experimental data of the extracellular, anionic polysaccharide gellan in dilute solution. Our theoretical calculations agree very well with the experimental data. Furthermore, the interpretation of the initial decay rate of the dynamic structure factor as a characteristic frequency in the sense of dynamic scaling is discussed. As a result of our calculations, the influence of polydispersity on the shape of the dynamic structure factor at large scattering vectors is found to be small.

Introduction

Gellan is a linear, extracellular, anionic polysaccharide that exhibits unique properties in solution and gel. It has been the subject of many experimental studies like chiroptical, calorimetric, conductometric, and viscometric measurements and scattering techniques.[1−6] The primary structure of gellan in its ordered form has been elucidated by X-ray scattering measurements by Chandrasekaran et al.[4] From their analysis the authors came to the conclusion that gellan forms a 3-fold intertwined double helix. The equilibrium and dynamic properties of gellan in dilute solution have been investigated by static and dynamic light scattering.[5] The static structure factor was described by Koyama's theory for wormlike chains.[7] However, for the normalized initial decay rate of the dynamic structure factor there is no adequate description. Neither a rigid-rod model[8] nor a sliding-rod model[9] accounts for the observed dependence (cf. Figure 13 of ref 5). Similar disagreement was obtained for the extracellular polysaccharide of *Rhizobium trifolii* strain TA-1[5] and the bacterial polysaccharide xanthan.[10] There is general agreement that an adequate theoretical description of the dynamics of polysaccharides in dilute solution is still missing.[5,10,11] Recently, we presented a detailed theoretical study of the dynamic structure factor of semiflexible macromolecules in dilute solution.[12] The comparison of our theoretical calculations with quasielastic neutron and dynamic light scattering measurements on various natural and synthetic macromolecules like denatured ovalbumin, DNA, F-actin, and polystyrene in dilute solution exhibits good agreement.[12] The initial decay rate of the dynamic structure factor of macromolecules in solution has also been calculated and compared with experimental data.[13] Furthermore, the incoherent and coherent dynamic structure factor of macromolecules in a melt have been investigated in terms of our model presented in refs 14 and 15. The comparison of our theoretical calculations with quasielastic neutron scattering experiments on different macromolecules in a melt also exhibits good agreement.[16] In summary, our model calculations describe dynamical properties of semiflexible macromolecules both in dilute solution and in a melt, in correspondence with experimental data. Furthermore, equilibrium properties of our model, e.g., the mean square radius of gyration r_g^2 agree with those of the Kratky-Porod model.[17]

Consequently, we expect that a study of the dynamics of polysaccharides in dilute solution in terms of our model will overcome the deficiencies of the rigid-rod model and the sliding-rod model in describing experimental data. In the following, our model calculations are compared with experimental data obtained from dynamic light scattering experiments on gellan in dilute solution.

Results and Discussion

According to our model the dynamic structure factor of semiflexible macromolecules in dilute solution is given by[12]

$$S(\mathbf{q},t) = \frac{e^{-q^2Dt}}{L^2}\int_{-L/2}^{L/2}\int_{-L/2}^{L/2} ds\, ds' \exp\left(-\frac{q^2}{6}a(s-s')\right) \times \exp\left(-\frac{q^2 k_B T}{3\pi\eta}\sum_{l=1}^{\infty}\tau_l\psi_l(s)\,\psi_l(s')(1-e^{-t/\tilde{\tau}_l})\right) \tag{2.1}$$

with

$$a(s-s') = \frac{|s-s'|}{p} - \frac{1}{2p^2}(1-e^{-2p|s-s'|}) \tag{2.2}$$

where D is the translational diffusion coefficient that exhibits a length dependence $D \sim 1/\sqrt{L}$ for flexible macromolecules and $D \sim \ln L/L + const/L$ for stiff macromolecules. L is the length and $1/(2p)$ is the persistence length of the macromolecules. The temperature T and viscosity η characterize the solvent. $\psi_l(s)$ are the eigenfunctions 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 stretching to bending modes with increasing mode number l on small length scales, even for very flexible macromolecules, due to finite chain stiffness. The stretching modes agree with those of the well-known Rouse model.[18] 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 slightly bending rod model of Aragón and Pecora.[19] The first relaxation time τ_1, which is often called the rotational relaxation time, exhibits for very

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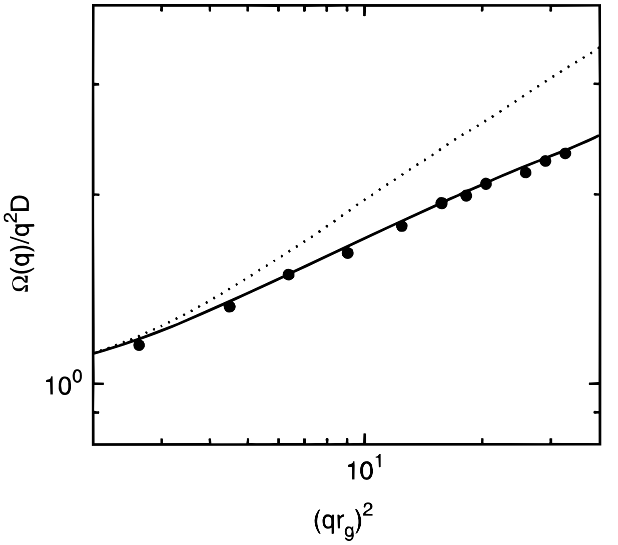

Figure 1. Log–log plot of the normalized initial decay rate for a semiflexible macromolecule of length $L = 611$ nm and of persistence length $1/(2p) = 161$ nm computed according to eq 2.4. The circles display experimental data on gellan in dilute solution.[5] The dotted line represents the theoretical calculation for pDS1-DNA in dilute solution.[12] The model parameters of pDS-DNA are $L = 1325$ nm and $1/(2p) = 66$ nm.[21]

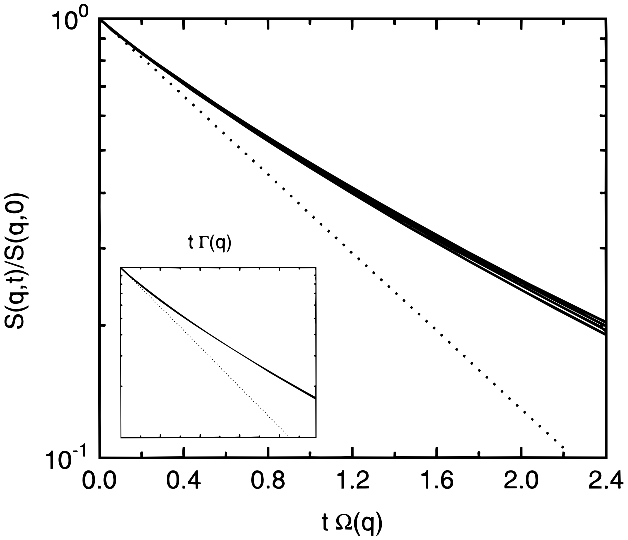

Figure 2. Normalized dynamic structure factor $S(\mathbf{q},t)/S(\mathbf{q},0)$ plotted versus the scaling variable $t\Omega(\mathbf{q})$ for different scattering vectors: $qr_g = 3, 4, 5,$ and 6. The scattering vector increases from bottom to top. The curves are computed according to eqs 2.1 and 2.4, where the length and the persistence length were fixed to $L = 611$ nm and $1/(2p) = 161$ nm, respectively. The insert displays the scaling behavior of the dynamic structure factor if $S(\mathbf{q},t)/S(\mathbf{q},0)$ is plotted versus the scaling variable $t\Gamma(\mathbf{q})$ according to eq 2.3. The dotted lines represent single exponential functions.

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] It is found that the influence of the hydrodynamic interaction on the relaxation times for semiflexible macromolecules becomes more and more important with both increasing chain flexibility and increasing mode number l. In evaluating the dynamic structure factor according to eq 2.1, we found that at scattering vectors larger than the inverse persistence length the stiffness of the macromolecules is important for any kind of macromolecules, i.e., even for very flexible ones. Both the shape of the dynamic structure factor and the decay rate $\Gamma(\mathbf{q})$ of the dynamic structure factor defined by

$$\frac{S(\mathbf{q},t = \Gamma^{-1}(\mathbf{q}))}{S(\mathbf{q},0)} = \mathrm{e}^{-1} \tag{2.3}$$

differ from the results known for flexible macromolecules. In particular, we found a weaker q dependence of $\Gamma(\mathbf{q})$ as predicted by the Rouse–Zimm model for flexible macromolecules. For more details concerning our model calculations and a comparison with other theoretical approaches, the reader is referred to ref 12.

In Figure 1 we present the computed normalized initial decay rate

$$\frac{\Omega(\mathbf{q})}{q^2D} = -\lim_{t\to 0}\frac{\mathrm{d}}{\mathrm{d}t}\frac{\ln(S(\mathbf{q},t))}{q^2D} \tag{2.4}$$

for a semiflexible macromolecule of length $L = 611$ *nm* and of persistence length $1/(2p) = 161$ nm in dilute solution. Figure 1 also displays experimental data on gellan.[5] The molecular parameters of gellan, i.e., the contour length $L = 611 \pm 9$ nm, and the persistence length $1/(2p) \approx 161$ nm, are obtained from static light scattering[5] using the Koyama expression. The persistence length of gellan is not known exactly. A 10% variation of the persistence length used in our calculation would change the results in Figure 1 by less than 2%. As is apparent from Figure 1, the comparison of our theoretical calculations with the experimental data exhibits very good agreement. At scattering vectors $qr_g > 2$ the relation $\Omega(\mathbf{q}) \sim q^{2.56}$ is approximately valid. This q dependence of $\Omega(\mathbf{q})$ differs from the predictions of both the rigid-rod model[8] and the sliding-rod model,[9] as shown in Figure 13 of ref 5.

The dotted line in Figure 1 represents the theoretical calculation for pDS1-DNA in dilute solution, which agrees well with experimental data on pDS1-DNA shown in ref 12. The model parameters of pDS1-DNA are $L = 1325$ nm and $1/(2p) = 66$ nm;[21] i.e., pDS1-DNA is more flexible than gellan. As is obvious from Figure 1, information on the stiffness of macromolecules can be obtained from the normalized initial decay rate of the dynamic structure factor. In particular, a different q dependence of $\Omega(\mathbf{q})$ is observed for gellan than for pDS1-DNA. We like to emphasize that the observed q dependence is a consequence of the fact that all internal modes contribute to the dynamic structure factor and cannot be described by, e.g., bending modes only.

In order to clarify whether the initial decay rate $\Omega(\mathbf{q})$ and/or the decay rate $\Gamma(\mathbf{q})$ can be considered as characteristic frequencies in the sense of dynamic scaling, $S(\mathbf{q},t)/S(\mathbf{q},0)$ is plotted for various scattering vectors ranging from $qr_g = 3$ to $qr_g = 6$ versus the scaling variable $t\Omega(\mathbf{q})$ in Figure 2. Additionally, the insert in Figure 2 displays the dynamic structure factor as a function of the scaling variable $t\Gamma(\mathbf{q})$. Obviously, the dynamic structure factor is rather a universal function of $t\Gamma(\mathbf{q})$ than of $t\Omega(\mathbf{q})$. In general, the characteristic frequency of the dynamic structure factor should be discussed in terms of the decay rate. In most of the theoretical investigations of the dynamics of semiflexible macromolecules performed so far the initial decay rate of the dynamic structure factor is calculated as an equilibrium average over the molecular conformations.

As noted by Stockmayer and Burchard,[22] the characterization of the dynamic structure factor by the initial decay rate only may be dangerous. We like to emphasize that the shape of our calculated curves are in full accordance with the experimental data presented in Figure 5 of ref 5. The dotted lines in Figure 2 display single exponential functions. The deviations of the theoretical calculations from the single exponential function are due to the intramolecular dynamics.

So far, polydispersity has not been taken into account in our theoretical calculations. As pointed out, polydispersity is expected to have only a little effect on the shape of the dynamic structure factor, because only internal modes of motion contribute to the dynamic structure factor at scattering vectors investigated in the experiment.[5] In general, for a solution containing macromolecules of different molecular weights the dynamic structure factor is given by[23]

$$S_z(\mathbf{q},t) = \frac{\int_0^\infty \mathrm{d}L\ S(\mathbf{q},t)\ w(L)L}{\int_0^\infty \mathrm{d}L\ w(L)L} \tag{2.5}$$

where $w(L)$ is the length distribution. Thus the dynamic structure factor has to be calculated as a function of contour length and the result then averaged over the length distribution. In polymer physics Schulz−Zimm distributions and logarithmic distributions are usually used.[24] In order to study the polydispersity effect on the experimental data on gellan in dilute solution, we calculate the dynamic structure factor for various contour lengths ranging from $L = 350$ nm to $L = 1000$ nm. In accordance with the presumption of Dentini et al.[5] we found only a little effect on the shape of the dynamic structure factor at scattering vectors $qr_g > 2$. Thus, local motion on small length scales is independent of contour length. Of course, polydispersity influences the shape of the dynamic structure factor at small scattering vectors where translational diffusion is dominant. A detailed study of the influence of polydispersity on dynamic light scattering will be presented elsewhere.

We conclude that the dynamic light scattering data of gellan in dilute solution are well described by our model calculations. This result is particularly important for the interpretation of dynamic light scattering measurements of other polysaccharides like the bacterial polysaccharide xanthan, the extracellular polysaccharide of *R. trifolii* strain TA-1, and carboxylated derivatives of tamarind seed polysaccharide.

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